SYNTHESIS AND CHARACTERIZATION OF AMINE ISOCYANOBORANE COMPLEXES OF RUTHENIUM(II) AND IRON(II)

BY

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To determine the effectiveness of amine isocyanoboranes as ligands, several isocyanoborane complexes of the form [Fe(1,10-phenanthroline)$_2$(CNBH$_2$Amine)$_2$](PF$_6$)$_2$, [Fe(2,2'-bipyridine)$_2$(CNBH$_2$Amine)$_2$](PF$_6$)$_2$, and [Ru(2,2'-bipyridine)$_2$(CNBH$_2$Amine)$_2$](PF$_6$)$_2$ were synthesized and their properties investigated. These complexes were prepared via a two step reaction sequence. First, an amine iodoborane was reacted with the appropriate neutral cyano complex, Fe(1,10-phenanthroline)(CN)$_2$, Fe(2,2'-bipyridine)(CN)$_2$, or Ru(2,2'-bipyridine)(CN)$_2$ to yield the iodide complexes; [Fe(1,10-phenanthroline)$_2$(CNBH$_2$Amine)$_2$]I$_2$, [Fe(2,2'-bipyridine)$_2$-(CNBH$_2$Amine)$_2$]I$_2$, and [Ru(2,2'-bipyridine)$_2$(CNBH$_2$Amine)$_2$]I$_2$, respectively. These iodide complexes were then converted into the final products by either the action of AgPF$_6$ or NH$_4$PF$_6$.

Additional complexes were prepared by reaction of $[Fe(1,10\text{-phenanthroline})_2(CNBH_2trimethylamine)_2](PF_6)_2$ with either bromine or chlorine to yield complexes of the type $[Fe(1,10\text{-phenanthroline})_2(CNBX_2trimethylamine)_2](PF_6)_2$ with X being either Br or Cl.

These isocyanoborane complexes have a wide range of solvolytic stability. The complex, $[Fe(1,10\text{-phenanthroline})_2(CNBCl_2trimethylamine)_2](PF_6)_2$ can be recrystallized from refluxing water-acetonitrile mixtures while the complexes $[Fe(2,2'\text{-bipyridine})_2(CNBH_2dimethylamine)_2](PF_6)_2$, and $[Fe(1,10\text{-phenanthroline})_2(CNBBr_2trimethylamine)_2](PF_6)_2$ decompose at room temperature in methanol in one to two hours. The coordination of the amine borane group to the cyano ligand in a complex can be reversed. Controlled solvolysis reactions using methanol were used to decompose coordinated amine isocyanoboranes ligands to yield complexes with the original cyano ligands intact.

The conversion of a cyano ligand into an amine isocyanoborane ligand produces profound electronic changes in the metal complex. Coordination of the amine borane group to the cyano ligand causes a stabilization of the π^* orbitals of the CN ligand which in turns leads to more favorable d_π-π^* interactions between the metal ion and the CN ligand and a lowering of the d_π orbital energies. This stabilization of the metal orbitals was reflected in a shift of the absorption maximum in the electronic spectrum of the amine isocyanoborane complexes relative to the uncomplexed

cyano compounds. In additional, the stabilization of the metal orbitals resulted in a shift to more positive potentials for the $E_{\frac{1}{2}}$ for the $M^{+3/+2}$ couple. Halogenation of the boron further enhanced the stabilization effect and produced still more positive $E_{\frac{1}{2}}$ potentials.

Although amine isocyanoboranes may never supplant organic isonitrile as ligands in transition metal complexes, they do constitute an attractive and effective alternative.

CHAPTER 1

INTRODUCTION

Credit is generally given to Gautier and Hofmann for the discovery of isocyanides (R-N≡C), although several isocyanides are now recognized as having been prepared earlier.[1,2] In 1867, Gautier[3,4] succeeded in preparing alkyl isocyanides by the treatment of alkyl iodides with silver cyanide, i.e.,

$$R\text{-}X + AgCN \longrightarrow AgX + R\text{-}NC.$$

At the same time Hofmann[5] also synthesized several alkyl isocyanides by reacting primary amines with chloroform and potassium hydroxide, i.e.,

$$R\text{-}NH_2 + CHCl_3 + 3\ KOH \longrightarrow R\text{-}N{\equiv}C + 3\ KCl + 3\ H_2O.$$

These reports sparked a virtual explosion of research which continues to this day in organo-isonitrile chemistry.[6] Today, organic isocyanides, or as they are called as a general class of compounds, isonitriles, are easily prepared by these and newer techniques, such as the dehydration of formamides. Isonitriles are of interest because they are useful intermediates in the syntheses of many organic and biochemical compounds, including peptides.[6]

Currently, organo-isocyanides are also finding widespread use in coordination chemistry.[6-10] Like carbon monoxide, to which all isocyanides (both organic and nonorganic) are structurally and electronically similar,[11] isocyanides can bond to transition elements in low oxidation states where π type metal-ligand interactions are important. The empty, low energy π^* orbitals on the isocyanides can interact with the filled d-π orbitals on low oxidation state metals to reduce negative charge buildup on the metal (see Figure 1). It is interactions of this type which produce the great stability of these complexes.

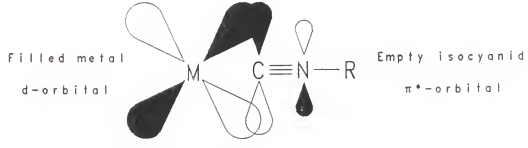

Figure 1. Metal-isocyanide π interaction.

Unlike CO, isocyanides also bond with high oxidation state transition elements. The structure of isocyanides (R-NC) is such that a high electron density is centered on the carbon atom (a "lone pair" in the valence bond description, i.e., R-N≡C:). This electron distribution results in a significantly higher dipole moment of around 3.5 D for isocyanides than in carbon monoxide ($\mu \approx 0.1$ D). Therefore, isocyanides exhibit a substantial σ-donor

capability which helps stabilize metals in high oxidation states. The presence of a variable R-group affords organoisocyanides an additional advantage over carbon monoxide. By altering the size and nature of the R-group, organoisocyanides can be exploited to produce complexes with varying steric and electronic environments.

The use of nonorganic isocyanide ligands (i.e., R_nX-NC, where X = noncarbon element and R = substituent on atom X), particularly other nonmetal isocyanides, offers the potential of even greater variation in the environment around the metal in coordination complexes. As with organic isocyanides, the environment produced by the isocyanide ligand can be altered by changes in the R-groups substituted on X. In addition, changes in coordination number and oxidation state of X itself as well as inductive effects produced by replacement of the R-groups by halogens can be used to further alter the steric and electronic effects. Of course, not all elements are expected to form stable free-isocyanides (i.e., where the carbon end of the isocyanide species is not coordinated to another atom).

The elements in groups IA and IIA, the alkali metals and alkaline earth metals, do not form stable free-isocyanides because their respective cyanides are, in fact, ionic. In these solids, the orientation of the CN^- ion is highly disordered even at low temperatures.[12] In solution, these salts dissociate completely into M^{+n} and CN^- ions or exist as ion-pairs rather than as bound cyanides or

isocyanides. Many of the transition and inner transition elements form CN^- compounds, which do not dissociate readily, but they form only stable cyano complexes because the barrier to isomerization (from M-N≡C to the more stable M-C≡N) is very low.[13]

Thus, only the less metallic elements (i.e., the nonmetal and metalloid elements such as B, Al, Ga, Si, Ge, As, etc.) with their higher kinetic barriers to isomerization might realistically be expected to form stable free-isocyanides. There has been, however, some difficulty in determining whether organometallic and organometalloid compounds which contain the C≡N moiety really have the isocyanide (M-N≡C) or the normal cyanide (M-C≡N) structure.[14]

The physical properties (e.g., melting points, volatilities, etc.) of the simple metalloid cyanides such as $Ge(CN)_4$ and $As(CN)_3$, suggest that most are polymeric, presumably with CN bridges. Several organometalloid compounds of Al, Ga, and In have been shown to be tetrameric in nature, again with CN bridges.[15] However, vibrational data on group IIIA organometalloid salts such as $[(CH_3)_4N][R_3GaCN]$, $K[(CH_3)_2Ga(CN)_2]$ and $[(CH_3)_4N][R_3TlCN]$ suggest that they are not polymeric but indicate the presence of C-bonded cyanide ligands.[16-20]

The structures of many alkyl derivatives of silyl and germyl cyanides are not certain. These covalent materials have been alternately proposed as cyanides, isocyanides, and

as mixtures of the cyanide and isocyanide derivatives. Attempts at structure elucidation based on chemical evidence have been made and arguments for the isocyanide structure in certain CN-containing silanes have been put forward.[21] The principal chemical evidence for the isocyanide structure being the reaction of $(CH_3)_3Si(CN \text{ or } NC)$ with sulfur to form the isothiocyanate (Eq. 1) which is analogous to the reactions of organo-isonitriles.[22]

$$(CH_3)_3SiNC + 1/8\ S_8 \longrightarrow (CH_3)_3SiNCS \qquad \text{(Eq. 1)}$$

While this reaction is most easily explained in terms of the isocyanide, these arguments clearly fail to consider the possibility that the reaction could take place by rearrangement of the normal cyanide with the formation of the isocyanide as a transient intermediate as in Eq. 2.

$$(CH_3)_3SiCN \longrightarrow [(CH_3)_3SiNC] \xrightarrow{1/8\ S_8} (CH_3)_3SiNCS \qquad \text{(Eq. 2)}$$

Moreover, the reaction could conceivably take place by formation of the thiofulminate followed by rearrangement to the isothiocyanate (Eq. 3).

$$(CH_3)_3SiCN \xrightarrow{1/8\ S_8} [(CH_3)_3SiCNS] \longrightarrow (CH_3)_3SiNCS \qquad \text{(Eq. 3)}$$

Other reaction sequences aimed at structure determination lead to similar ambiguous results.[23]

An equilibrium between the cyanide and isocyanide forms of $(CH_3)_3SiCN$ was proposed[24] based on the presence of two

infrared bands in the C≡N stretching region; one of relatively weak intensity at ≈ 2100 cm^{-1} and a second band of much higher intensity at ≈ 2190 cm^{-1}. Recently, detailed isotopic studies using ^{13}C and ^{15}N enriched samples have provided very convincing evidence to support the equilibrium theory.[14,25,26] The calculated and observed isotopic shifts of the ν_{CN} modes of $(CH_3)_3SiCN$ and $(CH_3)_3SiNC$ are in excellent agreement. A detailed analysis of the variable temperature vapor-phase IR spectra showed that the cyano isomer predominated and gave a value for the standard enthalpy change (ΔH°) of 4.00 ± 0.03 kcal/mole for the reaction

$$(CH_3)_3SiCN \longrightarrow (CH_3)_3SiNC$$

Similar equilibria have been found in triethylcyanosilane and triisopropylcyanosilane.[24,27] The analysis of the infrared spectra of ^{13}CN enriched samples of $(CH_3)_2Si(CN)_2$ revealed an equilibrium between the two linkage isomers $(CH_3)_2Si(CN)_2$ and $(CH_3)_2Si(CN)(NC)$.[28] Even the IR spectrum of $(CH_3)_3GeCN$ has been interpreted as an equilibrium between the cyano and isocyano forms.[22,29] However, without detailed isotopic studies, infrared spectroscopy usually does not provide an unequivocal structural criterion. In the IR spectrum, the CN stretching band for organic isonitriles typically appears at a slightly lower frequency than the corresponding nitrile (≈ 2150 cm^{-1} for the isonitrile vs. ≈ 2250 cm^{-1} for the nitrile). This difference is often used in an attempt to distinguish[30,31]

organic nitriles from organic isonitriles. However, organometallic and organometalloid CN derivatives[23] show a larger spread of CN and NC stretching frequencies than their organic counterparts. Consequently, when only a single isomer exists the position of the CN stretching frequency can not be used to determine the CN bonding mode.

As in the case with organo-isonitrile/nitriles, infrared spectroscopy can be useful in distinguishing between structural forms when both organometallic or organometalloid CN isomers exist. In 1970 Wade et al.[32] reported that when sodium borohydride, $NaBH_4$, was slurried with a solution of hydrocyanic acid (HCN) in tetrahydrofuran, the initial reaction produced a mixture of the salts, sodium cyanoborohydride ($NaBH_3CN$) and sodium isocyanoborohydride ($NaBH_3NC$). This conclusion was based on the observation of two CN stretching bands in the infrared spectrum, one at $\approx$ 2180 cm^{-1} and the other at $\approx$ 2070 cm^{-1}, which were assigned to the cyano and isocyano derivatives, respectively. When the system was refluxed, the band at $\approx$ 2070 cm^{-1} disappeared while the band at $\approx$ 2180 cm^{-1} grew in intensity. This was taken as evidence for the isomerization of the isocyanoborohydride ion, BH_3NC^-, into the cyanoborohydride ion, BH_3CN^-. The instability of sodium isocyanoborohydride was supported by the fact that it could not be isolated pure.

More recently Vidal and Ryschkewitsch[33-35] reported the synthesis of trimethylamine-isocyanoborane ($TMABH_2NC$) by

reacting silver cyanide with trimethylamine-iodoborane ($TMABH_2I$). Once again the structural assignment was based on infrared spectroscopic evidence. The isolated, pure product had a CN stretching frequency at $\approx 2135\ cm^{-1}$. This is some $50\ cm^{-1}$ lower than the CN stretching frequency of $\approx 2185\ cm^{-1}$ reported[36,37] for trimethylamine-cyanoborane ($TMABH_2CN$). Despite the large number of reported coordination compounds with isocyanides as ligands (i.e., with bridging CN groups), trimethylamine-isocyanoborane represents the only noncarbon free-isocyanide isolated to date.

Due to the above-mentioned paucity of free nonorganic isocyanides, it is not surprising that the isocyanide-containing coordination compounds that have been reported, typically, are not formed by reaction of a free isocyanide-containing ligand with the metal center. Instead, they involve the formation of an anionic isocyanide ligand generated <u>in situ</u> by reaction of a cyanide ion, already coordinated to the metal and a Lewis acid, AX_m,

$$(L)_nM\text{-}CN + AX_m \longrightarrow (L)_nM\text{-}CN\text{-}AX_m ,$$

where A is usually boron but can be any group IIIA or IVA element and where X is a hydrogen, an alkyl group, or a halogen. The only reported nonorganic isocyanide complex synthesized from a free isocyanide is the complex, $Mn(CO)_4Br(CNBH_2N(CH_3)_3)$, synthesized by Ryschkewitsch and

Vidal[27] from $Mn(CO)_5Br$ and $CNBH_2N(CH_3)_3$, trimethylamine-isocyanoborane.

In principle, any Lewis acid can be used to convert a coordinated cyanide ligand [i.e., M-(CN)] into an isocyanide ligand [i.e., M-(CN-X)] by complexation at the nitrogen, but the use of boron Lewis acids offers some interesting possibilities. Lewis acids of boron with their tendency to form strong bonds to nitrogen donors (an attribute important in the stability of CN-B moieties) not only afford the possibility of formation of four-coordinate anionic isocyanide ligands such as $CN-BF_3^-$, but three- and four-coordinate neutral (e.g., $CN-BR_2$ and $CN-BR_2L$) and cationic (e.g., $CN-BRL_2^+$ and $CN-BL_3^{+2}$) species as well. For example, Shriver[40-42] has reported on a series of Fe, Ni, and Mo complexes prepared from metal cyanides and group IIIA and IVA Lewis acids including BF_3, BCl_3, and BBr_3 (in which the isocyanide linkage was assumed). Manzer and coworkers[43,44] demonstrated that the addition of boron Lewis acids to coordinated cyanides does indeed produce the C≡N-B linkage in certain Pt complexes. The linkage in the product, trans-$HPt(PEt_3)_2\underline{CN}-BR_3$, was confirmed by comparison with the isomer, trans-$HPt(PEt_3)_2\underline{NC}-BR_3$, which was independently synthesized. Similarly, Purcell[45] reported the synthesis of the octahedral complex, cis-Fe(1,10-phenanthroline)$_2(\underline{CN}BH_3)_2$ and its linkage isomer, cis-Fe(1,10-phenanthroline)$_2(\underline{NC}BH_3)_2$. Complexes with neutral boron isocyanide ligands have also been prepared. The previously mentioned $Mn(CO)_4Br(CNBH_2N(CH_3)_3)$

prepared. The previously mentioned $Mn(CO)_4Br(CNBH_2N(CH_3)_3)$ features the $CNBH_2N(CH_3)_3$ ligand as does the complex $Fe(Cp)(CO)_2CNBH_2N(CH_3)_3$ prepared by Ryschkewitsch and Mathur[46] from $Fe(Cp)(CO)_2CN$ and $(CH_3)_3NBH_2I$. More recently, an intriguing series of pentacarbonylisocyanoborane-chromium(0) complexes was synthesized by Höfler and Löwenich[47] which involved three-coordinate neutral boron isocyanide ligands. These examples illustrate the potential for boron isocyanides as ligands but represent only a beginning for by further derivatization at the boron center such as halogenation, the synthesis of a nearly endless variety of boron isocyanide ligands should be possible.

The purpose of this work was to investigate the potential of amine isocyanoboranes ($CNBH_2NR_3$) as ligands in transition metal complexes. Although a large variety of boron isocyanide ligands are imaginable, amine isocyanoboranes were chosen for this study as they are neutral and thus, are both structurally and electronically analogous to organic isonitriles. To ascertain the efficacy of the amine isocyanoboranes as ligands a series of transition metal complexes was synthesized containing amine isocyanoborane ligands and their spectroscopic and electrochemical properties were determined.

Due to the paucity of free isocyanoboranes (vide supra), complexes containing these ligands were not be synthesized from the free isocyanides. Instead they were synthesized by conversion of existing cyano complexes by

alkylation of a cyano complex by alkyl iodides. To minimize the hazard of cyanide ligand loss during synthesis, the robust low spin d^6 complexes, Ru(2,2'-bipyridine)$(CN)_2$, Fe(2,2'-bipyridine)$(CN)_2$, and Fe(1,10-phenanthroline)$(CN)_2$, were used.

CHAPTER 2

MATERIALS AND PROCEDURE

2.1 Materials

All solvents were obtained from Fisher Scientific as reagent grade chemicals and were dried by standard published procedures.[48] The solvents were distilled under nitrogen using a four-foot fractionating column with the middle 70 percent collected. The purified solvents were stored in a dry box. The methanol used in the chromatography was HPLC grade also obtained from Fisher Scientific and used without further purification.

A sample of $[Ru(bipy)_3]I_2$ was obtained from Dr. Ernest F. Stine and was used without further purification. Trimethylamine-borane (TMA-borane) and dimethylamine-borane (DMA-borane) were obtained from Callery Chemical Corporation and Aldrich Chemical Company, respectively, and samples were sublimed immediately before use. Tetrahydrofuran-borane was reacted with 4-methylpyridine (4-picoline, 4-Pic) to produce the compound, 4-methylpyridine-borane (4-Pic-borane). The product was recrystallized from a benzene-heptane mixture before use. Trimethylamine-iodoborane was prepared *in situ* as described by Ryschkewitsch and Wiggins[49] but using methylene chloride as the solvent. Using similar

procedures, dimethylamine-iodoborane and 4-methylpyridine-iodoborane were prepared. Trimethylamine-cyanoborane and trimethylamine-isocyanoborane were synthesized by published procedures.[34,35,50]

All other chemicals were reagent grade and were used without further purification.

2.2 Procedures

All nonaqueous reactions were carried out in a nitrogen purged flow box at room temperature unless specified otherwise. All aqueous reactions were run in a well-ventilated fume hood. A Vacuum Atmosphere dri-train model dry box was used for storage and handling of all moisture sensitive materials.

All samples were analyzed for C, H, and N using departmental staff and equipment, Galbraith Laboratories, Knoxville, Tennessee, or Atlantic Microlabs, Atlanta, Georgia.

Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer. The samples were prepared in a dry box and were run as methylene chloride solutions or as KBr pellets. The spectra were recorded under a nitrogen atmosphere.

Samples for NMR spectroscopy were prepared in a dry box in deuterated acetonitrile or in a flow box using deuterated methanol. The tubes were capped then sealed with Parafilm brand laboratory film and run immediately. Proton and ^{11}B NMR spectra were obtained at 300 MHz and 96 MHz,

respectively, on a Varian VXR 300 spectrometer at room temperature. The ^{1}H spectra were resolution enhanced using the RESOLV subroutine. The non-first-order ^{1}H spectra were analyzed using the SPINS and SPINI subroutines to obtain the reported chemical shifts and coupling constants.

The UV-VIS spectra were recorded in acetonitrile on a Perkin Elmer Lambda 6 UV-VIS spectrophotometer. The spectra were converted to data files and stored on disk. After scaling the data using the Quattro Pro program[51], the spectra were replotted using the Grapher[52] program. Cyclic voltammograms were recorded in acetonitrile with 0.1 M tetraethylammonium perchlorate as the supporting electrolyte using a Princeton Applied Research Model 175 Universal Programmer equipped with a Princeton Applied Research Model 176 Current Follower and a Princeton Applied Research Model 173 Potentiostat/Galvanostat with a platinum button working electrode and a silver/silver chloride reference electrode.

CHAPTER 3

EXPERIMENTAL

3.1 Syntheses and Characterizations of Precursors and Reference Compounds

3.1.1 Syntheses of Chloro Complexes

The complexes, cis-dichlorobis(1,10-phenanthroline)-iron(II) and cis-dichlorobis(2,2'-bipyridine)ruthenium(II), were synthesized as precursors to cyano or trimethylamine-cyanoborane complexes using modifications of existing procedures and were not fully characterized. These complexes were prepared in the atmosphere, dried under vacuum and transferred into a nitrogen flow-box for storage, prior to use.

3.1.1.1 Synthesis of cis-dichlorobis(1,10-phenanthroline) iron(II), cis-$Fe(phen)_2Cl_2$

The complex, cis-$Fe(phen)_2Cl_2$, was prepared in a two step synthesis from ferrous ammonium sulfate. First, the complex, tris(1,10-phenanthroline)iron(II) chloride hepta-hydrate was synthesized, then partially dehydrated and finally converted into the desired final complex, cis-$Fe(phen)_2Cl_2$.

The procedure of Akabori, Matsuo, and Yamamoto[53] for the synthesis of tris(1,10-phenanthroline)iron(II) chloride heptahydrate, $[Fe(phen)_3]Cl_2 \cdot 7H_2O$, was attempted. A mixture of 2.635 g (6.720 mmol) of ferrous ammonium sulfate hexahydrate, 4.0015 g (6.720 mmol) of 1,10-phenanthroline monohydrate and 250 mL of water were heated to 50°C and the mixture stirred until all solids had dissolved. According to instructions, thirty mL of saturated NaCl solution were added with stirring to the warm red solution but no precipitate formed even after cooling the mixture to room temperature. Thirty mL of saturated ammonium chloride solution were added in an attempt to induce precipitation but to no effect. The mixture was then rotary evaporated to dryness to give a mixture of NaCl, NH_4Cl, and the desired complex. This solid mass was extracted with 200 mL of methanol. After filtering to remove a large quantity of white solid, the filtrate was evaporated to dryness under vacuum. The extraction, filtration and evaporation procedures were repeated twice using methylene chloride as the extractant. After drying at 80°C for two hours under vacuum, the yield of partially hydrated tris(1,10-phenanthroline)iron(II) chloride was 4.848 g.

The complex, cis-dichlorobis(1,10-phenanthroline)-iron(II), has been reportedly synthesized by different procedures. Baker and Bobinich[54] prepared the complex by refluxing tris(1,10-phenanthroline)iron(II) chloride in nonpolar solvents, while Madeja, Wilke, and Schmidt[55]

reported the synthesis by heating tris(1,10-phenanthroline) iron(II) chloride under vacuum. The actual synthesis employed was a combination of these literature procedures. Following the procedure of Baker and Bobinich, a mixture of 4.582 g of the partially hydrated tris(1,10-phenanthroline) iron(II) chloride and 200 mL of CCl_4 were refluxed under nitrogen for 43 hours. After cooling to room temperature the mixture was transferred to a nitrogen flow box, filtered and the solid washed twice with 40 mL aliquots of fresh CCl_4. After drying the solid the yield was 3.777 g. The product was a blue solid with white flecks of what was later determined to be 1,10-phenanthroline. This crude solid was transferred to a vacuum oven where it was heated at 110°C for four hours. During this period the remaining 1,10-phenanthroline was sublimed away from the product and collected on the cooler window of the oven. The solid was heated for an additional two hours until no more 1,10-phenanthroline sublimed. After cooling the final yield of cis-dichlorobis(1,10-phenanthroline)iron(II) was 2.882 g or 93.15% based on ferrous ammonium sulfate. The elemental analysis for $C_{24}H_{16}N_4Cl_2Fe$ was:

Calcd: 59.17% C, 3.31% H, and 11.50% N.

Found: 58.81% C, 3,20% H, and 11.40% N

3.1.1.2 Synthesis of cis-dichlorobis(2,2'-bipyridine)-ruthenium(II), cis-$Ru(bipy)_2Cl_2$

Cis-dichlorobis(2,2'-bipyridine)ruthenium(II) was prepared by a modification of existing procedures.[56,57] A mixture of 4.04 g (15 mmol) of $RuCl_3 \cdot n\ H_2O$ (26% H_2O), 4.67 g (29.9 mmol) of 2,2'-bipyridine and 250 mL of an 80:20 ethylene glycol/ethanol solution were refluxed for one hour under a nitrogen atmosphere. The solvents were then removed under vacuum at 60°C. The resulting solid was mixed with 250 mL of a 50:50 ethanol/water solution, and the combination refluxed again for one hour. After cooling to 50°C the mixture was filtered to remove any undissolved solids. Twenty grams of LiCl were added, and the ethanol portion was removed by distillation until the vapor temperature reached 90°C. The resulting solution was placed in a refrigerator overnight during which time fine purple-black microcrystals formed. The crude product was isolated by filtration, rinsed with 250 mL of cold water (until the filtrate failed to fluoresce), and dried under vacuum at 80°C. The yield was 5.46 g.

Purification was achieved by refluxing the crude solid in 250 mL of a 50:50 ethanol/water solution for one hour, filtering to remove any remaining solids and cooling the mixture to 50°C. After the addition of 20 g of LiCl, the ethanol was again removed by distillation (until the vapor temperature reached 90°C) and the resulting mixture cooled in a refrigerator overnight. The purified product was

filtered, washed with 200 mL of cold water and dried overnight at 80°C. The yield was 4.96 g (68% overall).

3.1.2 Syntheses and Characterizations of Cyano Complexes

Using literature procedures, the complexes, cis-$Fe(phen)_2(CN)_2$, cis-$Fe(bipy)_2(CN)_2$, and cis-$Ru(bipy)_2(CN)_2$, were synthesized as precursors to amine-isocyanoborane and amine-cyanoborane complexes.

3.1.2.1 Synthesis of cis-dicyanobis(1,10-phenanthroline)-iron(II), cis-$Fe(phen)_2(CN)_2$

The compound, cis-$Fe(phen)_2(CN)_2$, was prepared by the method of Schilt.[58] A mixture of 12.01 g (66.64 mmol) of 1,10-phenanthroline, 7.80 g (19.9 mmol) of ferrous ammonium sulfate hexahydrate, and 800 mL of water was heated to 90°C in a 2L beaker. A solution of 20.0 g (310 mmol) of potassium cyanide in 50 mL of water was added with vigorous stirring and the mixture allowed to cool overnight. The crude product was isolated by filtration and the purple solid washed first with 500 mL of water, then with 50 mL of ethanol, and finally with 50 mL of diethyl ether. After drying under vacuum, the crude yield was 8.90 g.

When the recrystallization method described by Schilt was employed, a sample was produced which Galbraith Laboratories in Knoxville, Tenn. analyzed as 63.61% C, 4.08% H, 16.97% N and 12.46% Fe. These values are close to the C, H, and N analyses of the "dihydrate" reported by

Schilt but, differ somewhat from the 61.92% C, 4.00% H, 16.67% N, and 11.07% Fe calculated for the dihydrate. This material was nonhomogeneous when eluted with methanol on Sephadex LH-20 chromatographic resin, producing a pink-orange band ahead of the purple product band. In addition, this solid left an orange residue in a Soxhlet thimble after extraction with absolute ethanol. Consequently, an alternate purification procedure[59] to that of Schilt was employed.

The crude product was extracted with approximately 500 mL of absolute ethanol in a Soxhlet extractor under a nitrogen atmosphere until the filtrate was colorless (about one week). The volume of the filtrate was reduced to 300 mL by evaporation and the product isolated by filtration. After rinsing the solid with 50 mL of ethanol and then with 150 mL of diethyl ether, the product was dried under vacuum at 80°C. A methanol solution of this material was chromatographically homogeneous on Sephadex LH-20 resin. The yield was 8.03 g (86% yield overall). The elemental analysis for $Fe(phen)_2(CN)_2$ was:

Calcd: 66.69% C, 3.44% H, and 17.95% N.

Found: 66.58% C, 3.39% H, and 17.90% N.

3.1.2.2 Synthesis of cis-dicyanobis(2,2'-bipyridine)-iron(II), cis-$Fe(bipy)_2(CN)_2$

The compound, cis-$Fe(bipy)_2(CN)_2$, was also prepared by the method of Schilt.[58] A mixture of 11.7 g (29.8 mmol) ferrous ammonium sulfate hexahydrate, 14.0 g (89.6 mmol) of 2,2'-bipyridine, and 1L of water was heated to 95°C in a 2L beaker. A solution of 30.0 g (310 mmol) of potassium cyanide in 50 mL of water was added to the hot solution with vigorous stirring. The resulting mixture was allowed to cool overnight. The deep-purple solid which formed was filtered and washed first with 100 mL of water, then with 20 mL of acetone, and finally with 100 mL of diethyl ether. After drying in air, the yield of the crude product was 10.1 g.

As in the previous synthesis, an alternate purification scheme[59] was employed. The material was purified by extracting the crude product with 500 mL of absolute ethanol in a Soxhlet extractor under a nitrogen atmosphere until the filtrate was colorless (about one week). The volume of the filtrate was reduced to 250 mL by evaporation and the purified solid was isolated by filtration. After washing the purple solid with 50 mL of diethyl ether, the product was dried under vacuum at 60°C. The final yield was 7.1 g (57% yield overall). A methanol solution of this solid was chromatographically homogeneous on Sephadex LH-20 resin. The ^1H NMR of this solid in deuterated methanol showed no impurities. This material is hygroscopic and all

departmental elemental analyses showed varying degrees of hydration depending on length of exposure to the atmosphere. A typical analysis for $Fe(bipy)_2(CN)_2 \cdot H_2O$ was:

Calcd: 60.29% C, 4.14% H, and 19.17% N.

Found: 59.98% C, 3.84% H, and 19.08% N.

3.1.2.3 Synthesis of cis-dicyanobis(2,2'-bipyridine)-ruthenium(II), cis-$Ru(bipy)_2(CN)_2$

A modification[60] of the procedure of White and Ohnesorge[61] for the preparation of cis-$Ru(phen)_2(CN)_2$ was used to synthesize cis-$Ru(bipy)_2(CN)_2$. A mixture of 6.968 g (14.39 mmol) of cis-$Ru(bipy)_2Cl_2$, 15.0 g (306 mmol) of sodium cyanide, and 200 mL of water was refluxed under nitrogen for three hours. After cooling to room temperature, the mixture was filtered, and the red-orange solid washed first with water until the filtrate was only light yellow, then with 50 mL of cold ethanol, and finally with 100 mL of diethyl ether. The crude product was purified by first dissolving it in 500 mL of hot methanol to which 30 g of 60-200 mesh activated silica gel (Davison Chemical Co.) had been added to remove charged impurities. Then after refluxing for five minutes, the mixture was cooled to room temperature, filtered through a 1/4 inch layer of Celite, and the resulting clear, deep-red solution was evaporated to dryness. Finally, the recovered solid was recrystallized from 200 mL of hot methanol. After drying under vacuum at 60°C, the final overall yield of deep red

crystals was 3.923 g (58.57%). A methanol solution of this solid was chromatographically homogeneous on Sephadex LH-20 resin and the ^1H NMR in deuterated methanol of samples stored in a glove box showed no traces of water. The solid is, however hygroscopic and departmental elemental analyses showed varying degrees of hydration depending on length of exposure to the atmosphere. A typical analysis for cis-$Ru(bipy)_2(CN)_2 \cdot 1.5\ H_2O$ was:

Calcd: 53.65% C, 3.89% H, and 17.06% N.

Found: 53.61% C, 3.60% H, and 16.87% N.

3.1.2.4 Characterizations of Cyano Complexes

The cyano complexes, $Fe(1,10\text{-phenanthroline})_2(CN)_2$, $Fe(2,2'\text{-bipyridine})_2(CN)_2$ and $Ru(2,2'\text{-bipyridine})_2(CN)_2$, were characterized by IR and UV-VIS spectroscopy as well as ^1H NMR and cyclic voltammetry (vide supra). The IR spectra were obtained from samples in KBr pellets, but due to the hygroscopic nature of these compounds, it was difficult to obtain spectra free of water contamination. The individual spectra are shown in Appendix A. Their UV-VIS spectra, which exhibit a sizable solvent dependence were obtained from acetonitrile solutions. The wavelengths of maximum absorbance (λ_{max}) for the compounds are listed in Table 1 while the actual spectra are shown in Appendix B. Figures 2 and 3 include the general structures of the complexes and their lettering schemes for NMR purposes. The ^1H chemical shifts and coupling constants measured at 300 MHz for these

Table 1. Wavelength of maximum absorbance (λ_{max}) in the electronic spectra (330-750 nm) of the hexafluorophosphate complexes and related compounds in acetonitrile solution.

	λ_1 in nm	λ_2 in nm
$Fe(phen)_2(CN)_2$	598	---
$[Fe(phen)_3](PF_6)_2$	508	---
$[Fe(phen)_2(CNBH_2DMA)_2](PF_6)_2$	407	---
$[Fe(phen)_2(CNBH_2 4\text{-}Pic)_2](PF_6)_2$	410	---
$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$	404	---
$[Fe(phen)_2(CN)(CNBH_2TMA)](PF_6)$	507	---
$[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$	368	---
$[Fe(phen)_2(CNBBr_2TMA)_2](PF_6)_2$	368	---
$Fe(bipy)_2(CN)_2$	607	387
$[Fe(bipy)_3](PF_6)_2$	519	350
$[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	445	---
$[Fe(bipy)_2(CN)(CNBH_2DMA)](PF_6)$	516	345
$[Fe(bipy)_2(CNBH_2 4\text{-}Pic)_2](PF_6)_2$	444	---
$[Fe(bipy)_2(CNBH_2TMA)_2](PF_6)_2$	439	---
$Ru(bipy)_2(CN)_2$	496	344
$[Ru(bipy)_3](PF_6)_2$	450	---
$[Ru(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	378	---
$[Ru(bipy)_2(CNBH_2 4\text{-}Pic)_2](PF_6)_2$	378	---
$[Ru(bipy)_2(CN)(CNBH_2 4\text{-}Pic)](PF_6)$	426	---
$[Ru(bipy)_2(\underline{CN}BH_2TMA)_2](PF_6)_2$	376	---
$[Ru(bipy)_2(\underline{NC}BH_2TMA)_2](PF_6)_2$	436	---

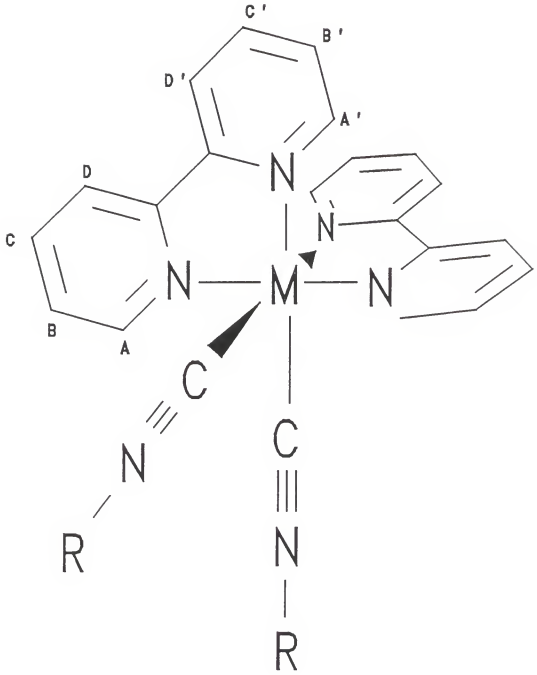

Figure 2. Lettering scheme of bipyridine complexes.

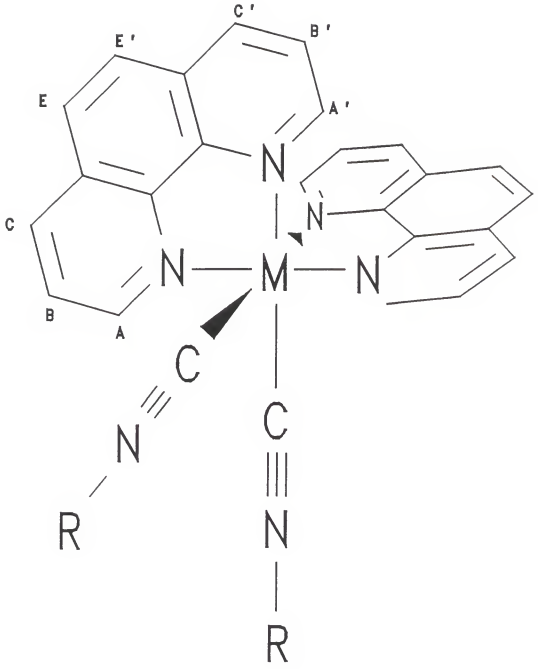

Figure 3. Lettering scheme of phenanthroline complexes.

complexes in deuterated acetonitrile solutions are listed in Tables 2 and 3, respectively. The $E_{\frac{1}{2}}$ values obtained from cyclic voltammetric measurements on the compounds in acetonitrile solutions are listed in Table 4.

3.1.3 Syntheses of Reference Complexes

3.1.3.1 Synthesis of Tris-(2,2'-bipyridine)iron(II) hexafluorophosphate, $[Fe(bipy)_3](PF_6)_2$

An excess of iron powder (approximately two-tenths gram), 0.337 g (1.33 mmol) of I_2, 0.70 g (4.8 mmol) of NH_4I and 0.756 g (4.84 mmol) of 2,2'-bipyridine were heated with stirring in 25 mL of methanol. After 10 minutes, the mixture was allowed to cool to room temperature, filtered to remove the excess iron, and the methanol removed by vacuum evaporation. The resulting solid was dissolved in methanol and chromatographed on Sephadex LH-20 resin using methanol as eluent. The deep-violet band was collected and the solvent removed under vacuum. After drying under vacuum overnight, the yield was 1.07 g.

A 0.408 g sample of this solid was dissolved in a mixture of 20 mL of methanol and 20 mL of water. An aqueous solution of NH_4PF_6 ($\approx$ 1 g in 10 mL) was slowly added while the mixture was stirred. After cooling in a freezer for three hours, the crude PF_6^- salt was filtered, washed with water and air dried. This solid was purified by heating it in 50 mL of methanol. When the mixture began to reflux,

Table 2. Proton chemical shifts of cyano complexes and related compounds (shifts in ppm).

Solvent = CD_3CN	δ_A	δ_B	δ_C	δ_D	δ_E	$\delta_{E'}$	$\delta_{D'}$	$\delta_{C'}$	$\delta_{B'}$	$\delta_{A'}$
1,10-phenanthroline	9.114	7.697	8.368	---	7.890	7.890	---	8.368	7.697	9.114
$Fe(phen)_2(CN)_2$*	9.994	7.968	8.594	---	8.149	8.070	---	8.359	7.377	7.488
$[Fe(phen)_3](PF_6)_2$	7.673	7.614	8.632	---	8.272	8.272	---	8.632	7.614	7.673
2,2'-bipyridine	8.660	7.380	7.882	8.421	---	---	8.421	7.882	7.380	8.660
$Fe(bipy)_2(CN)_2$	9.780	7.548	7.984	8.296	---	---	8.269	7.842	7.168	7.310
$[Fe(bipy)_3](PF_6)_2$	7.403	7.393	8.106	8.517	---	---	8.517	8.106	7.393	7.403
$Ru(bipy)_2(CN)_2$	9.697	7.625	8.026	8.359	---	---	8.294	7.864	7.216	7.595
$[Ru(bipy)_3](PF_6)_2$	7.737	7.402	8.061	8.504	---	---	8.504	8.061	7.402	7.737
Solvent = CD_3OD										
$Fe(phen)_2(CN)_2$	9.973	8.005	8.663	---	8.188	8.108	---	8.426	7.444	7.495
$Fe(bipy)_2(CN)_2$	9.665	7.601	8.069	8.457	---	---	8.431	7.924	7.258	7.317
$Ru(bipy)_2(CN)_2$	9.671	7.664	8.093	8.518	---	---	8.456	7.925	7.287	7.612

*Sample was run in CD_3CN which contained approximately 10% CD_3OD to improve solubility.

Table 3. Proton coupling constants for cyano complexes and related compounds. Constants in Hz.

	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}
Solvent = CD_3CN						
1,10-phenanthroline	4.31	1.78	----	8.10	----	----
$Fe(phen)_2(CN)_2$*	5.28	1.25	----	8.17	----	----
$[Fe(phen)_3](PF_6)_2$	5.26	1.27	----	8.27	----	----
2,2'-bipyridine	4.79	1.81	0.94	7.52	1.22	8.01
$Fe(bipy)_2(CN)_2$	5.72	1.56	0.81	7.54	1.41	8.10
$[Fe(bipy)_3](PF_6)_2$	5.69	1.49	0.80	7.62	1.35	8.15
$Ru(bipy)_2(CN)_2$	5.66	1.55	0.69	7.59	1.39	8.21
$[Ru(bipy)_3](PF_6)_2$	5.63	1.49	0.80	7.64	1.34	8.25
Solvent = CD_3OD						
$Fe(phen)_2(CN)_2$	5.28	1.32	----	8.19	----	----
$Fe(bipy)_2(CN)_2$	5.71	1.52	0.84	7.55	1.34	8.08
$Ru(bipy)_2(CN)_2$	5.68	1.56	0.82	7.61	1.35	8.23

*Sample was run in CD_3CN which contained approximately 10% CD_3OD to improve solubility.

Table 3. Continued.

$J_{EE'}$	$J_{A'B'}$	$J_{A'C'}$	$J_{A'D'}$	$J_{B'C'}$	$J_{B'D'}$	$J_{C'D'}$
----	4.31	1.78	----	8.10	----	----
8.92	5.19	1.25	----	8.21	----	----
----	5.26	1.27	----	8.27	----	----
----	4.79	1.81	0.94	7.52	1.22	8.01
----	5.62	1.51	0.82	7.55	1.34	8.10
----	5.69	1.49	0.80	7.62	1.35	8.15
----	5.51	1.55	0.84	7.61	1.29	8.21
----	5.63	1.49	0.80	7.64	1.34	8.25
8.96	5.21	1.32	----	8.19	----	----
----	5.61	1.52	0.81	7.55	1.27	8.11
----	5.50	1.59	0.83	7.60	1.30	8.23

Table 4. Peak potentials for isocyanide complexes in acetonitrile solution. Potentials in volts.

	E_{p_a}	E_{p_c}	ΔE_p	$E_{p_{\frac{1}{2}}}$
$[Fe(phen)_3](PF_6)_2$	1.16	1.07	0.09	1.12
$Fe(phen)_2(CN)_2$	0.58	0.51	0.07	0.54
$[Fe(phen)_2(CN)(CNBH_2TMA)](PF_6)$	1.04	0.93	0.11	0.99
$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$	1.52	1.41	0.11	1.47
$[Fe(phen)_2(CNBH_2DMA)_2](PF_6)_2$	1.45	1.33	0.12	1.39
$[Fe(phen)_2(CNBH_24\text{-Pic})_2](PF_6)_2$	1.48	1.40	0.08	1.44
$[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$	1.78	1.67	0.11	1.73
$[Fe(bipy)_3](PF_6)_2$	1.15	1.03	0.12	1.09
$Fe(bipy)_2(CN)_2$	0.58	0.42	0.17	0.50
$[Fe(bipy)_2(CN)(CNBH_2DMA)](PF_6)$	0.97	0.89	0.08	0.93
$[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	1.40	1.32	0.08	1.36
$[Fe(bipy)_2(CNBH_24\text{-Pic})_2](PF_6)_2$	1.44	1.36	0.08	1.40
$[Fe(bipy)_2(CNBH_2TMA)_2](PF_6)_2$	1.47	1.36	0.11	1.41
$[Ru)bipy)_3](PF_6)_2$	1.36	1.26	0.10	1.31
$Ru(bipy)_2(CN)_2$	0.89	0.82	0.07	0.86
$[Ru(bipy)_2(CN)(CNBH_24\text{-Pic})](PF_6)$	1.37	1.24	0.13	1.31
$[Ru(bipy)_2(CNBH_24\text{-Pic})_2](PF_6)_2$	1.86	1.70	0.16	1.78
$[Ru(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	1.80	1.66	0.14	1.73
$[Ru(bipy)_2(\underline{CN}BH_2TMA)_2](PF_6)_2$	1.90	1.76	0.14	1.83
$[Ru(bipy)_2(\underline{NC}BH_2TMA)_2](PF_6)_2$	1.50	1.32	0.18	1.41

acetonitrile was added dropwise until all of the solid had dissolved, then the solution was allowed to cool to room temperature. Further precipitation was induced by the addition of 30 mL of water and cooling overnight in a freezer. The purified $[Fe(bipy)_3](PF_6)_2$ was filtered, washed with water and dried under vacuum. The overall yield was 72.8%.

3.1.3.2 Synthesis of Tris-(2,2'-bipyridine)ruthenium(II) hexafluorophosphate, $[Ru(bipy)_3](PF_6)_2$

The crude salt was formed by the addition of a solution of NH_4PF_6 (1 g in 10 mL of water) to a solution of 0.500 g (0.607 mmol) of $Ru(bipy)_3I_2$ in 20 mL of water. The red-orange precipitate was filtered, washed with water and air dried. Purification was achieved by heating this solid in a mixture of 25 mL of water and 25 mL of methanol. When the mixture began to reflux, acetonitrile was added dropwise until all of the solid had dissolved. The resulting deep-red solution was allowed to cool to room temperature. Additional precipitation of the purified compound was induced by chilling the mixture overnight in a freezer. After filtering the solid, washing with water, and drying under vacuum at 70°C, the yield was 0.482 g (92.4% overall).

3.1.3.3 Synthesis of Tris-(1,10-phenanthroline)iron(II) hexafluorophosphate, $[Fe(phen)_3](PF_6)_2$

A mixture of 0.6610 g (1.686 mmol) of ferrous ammonium sulfate hexahydrate, 1.0110 g (5.100 mmol) of 1,10-phenanthroline monohydrate, and 75 mL of water were heated

to 60°C until all solids were dissolved. After cooling to room temperature, a solution of 1.0550 g (6.472 mmol) of NH_4PF_6 in 15 mL H_2O was added with vigorous stirring. A purple solid formed after the addition of a few drops of this solution. The crude product was filtered, washed first with 15 mL of water, then with 10 mL of diethyl ether, and dried under vacuum for one hour. The yield was 1.4780 g.

Purification was achieved by heating a mixture of the crude solid and 15 mL of methanol to reflux. Acetonitrile was slowly added to the refluxing mixture until all of the solid was dissolved. The purified product precipitated when this mixture was allowed to cool to room temperature. The solid was filtered, washed with methanol, and dried under vacuum to yield 0.9580 g of $[Fe(phen)_3](PF_6)_2$. A second crop was recovered by evaporation of the filtrate and recrystallization of the residue from a minimum volume of methanol/acetonitrile mixture. The combined yield was 1.3140 g (87.94% overall).

3.1.3.4 Synthesis of cis-bis(2,2'-bipyridine)-bis(trimethylamine-cyanoborane)ruthenium(II) hexafluorophosphate, cis-$[Ru(bipy)_2(NCBH_2TMA)_2](PF_6)_2$

A 0.094 g (0.96 mmol) sample of freshly sublimed trimethylamine-cyanoborane was dissolved in five mL of CH_2Cl_2. $Ru(bipy)_2Cl_2$ (0.113 g, 0.233 mmol) was added along with an additional five mL of CH_2Cl_2 to a stirred solution of the borane. Silver hexafluorophosphate (0.115 g,

0.455 mmol) was added and the mixture stirred for two and a half hours during which time the mixture turned red and much of the solid dissolved. After filtering off a small quantity of yellow-brown solid, 60 mL of diethyl ether were added dropwise to initiate precipitation of the desired complex. The orange solid was filtered, washed with 100 mL of diethyl ether and dried under vacuum to yield 0.202 g. Initial purification was achieved by dissolving the solid in 15 mL of methylene chloride, filtering off a small solid residue, and reprecipitating the product by the dropwise addition of 75 mL of diethyl ether. After drying under vacuum, the yield was 0.139 g.

This material was further purified by chromatography. A 0.070 g sample was mixed with four mL of 2:1 methanol/ acetonitrile solution and chromatographed on Sephadex LH-20 resin. The material eluted as a series of three bands; a leading pale dirty yellow band, then a large orange band and finally a trailing red-brown band. The bands were collected as 36 fractions using a fraction collector and the purity of the individual fractions monitored by UV-VIS spectroscopy. All of the orange fractions were combined and the solvents removed under a stream of nitrogen gas. After drying under vacuum, the yield was 0.53 g (66% overall). The analysis for $C_{28}H_{38}N_8B_2F_{12}P_2Ru$ was:

Calcd: 37.40% C, 4.26% H, 12.46% N.

Found: 37.88% C, 4.12% H, 12.39% N.

3.1.3.5 Synthesis of cis-bis(1,10-phenanthroline)-bis(trimethylamine-cyanoborane)iron(II) hexafluorophosphate, cis-$[Fe(phen)_2(NCBH_2TMA)_2](PF_6)_2$

A 0.116 g (1.18 mmol) sample of freshly sublimed trimethylamine-cyanoborane was dissolved in 15 mL of dry methylene chloride. $Fe(phen)_2Cl_2$ (0.247 g, 0.507 mmol) was added and the solid washed into the reaction mixture with 5 mL of CH_2Cl_2. Finally, 0.257 g (1.01 mmol) of $AgPF_6$ was added and the mixture stirred for one hour. The color of the mixture rapidly turned from the initial blue to an orange-red color with the deposition of a yellow solid (AgI). At the end of the stirring, the mixture was filtered to remove this solid and 25 mL of diethyl ether was added to the filtrate to induce precipitation of the product. The red-orange solid was filtered, washed with 25 mL of fresh ether and dried under vacuum. The isolated yield was 0.405 g. The analysis for $C_{32}H_{38}B_2F_{12}FeN_8P_2$ was:

Calcd: 42.61% C, 4.25% H, 12.42% N.

Found: 42.83% C, 3.76% H, 11.17% N.

3.1.3.6 Characterization of Complexes

The cis-$[Fe(phen)_2(NCBH_2TMA)_2](PF_6)_2$ proved to be highly unstable. This solid showed no visible stretches in the infrared spectrum from 2000-2300 cm^{-1} (a similar ruthenium product showed only a weak absorption in this region, vide infra) and had a λ_{max} at 467 nm in the UV-VIS spectrum when dissolved in acetonitrile. The absorption

band changed shape and shifted to 508 nm on standing in acetonitrile solution for 15 minutes indicating its conversion to $[Fe(phen)_3](PF_6)_2$. This change was confirmed by NMR, run on a sample of the original product in acetonitrile which had been left standing for 30 minutes.

The infrared spectra of the remaining complexes are shown in Appendix A. Their C≡N and B-H stretching frequencies are listed in Tables 5 and 6, respectively. The ^1H chemical shifts and coupling constants obtained for these complex in deuterated acetonitrile solutions are listed in Tables 7 and 8, respectively. Table 9 contains the ^{11}B chemical shifts measured at 96 MHz. These complexes were further characterized by cyclic voltammetry. The $E_{\frac{1}{2}}$ values obtained from the cyclic voltammograms in acetonitrile solution are listed in Table 4.

3.2 Syntheses and Characterizations of Bis(amine-isocyanoborane) Complexes

3.2.1. Syntheses of Bis(amine-isocyanoborane) Iodide Complexes

The complexes $[Fe(1,10\text{-phenanthroline})_2(CNBH_2amine)_2]I_2$ and $[M(2,2\text{-bipyridine})_2(CNBH_2amine)_2]I_2$ (where M is Fe and Ru), were prepared according to Equation 4 by reacting the appropriate metal cyanide complex with a solution of an amine-iodoborane prepared *in situ*:[49]

Table 5. C≡N stretching frequencies of hexafluorophosphate salts in methylene chloride solution. (frequencies in cm^{-1}).

	Symmetric	Asymmetric
$Fe(phen)_2(CN)_2$	2079.9	2065.2
$[Fe(phen)_2(CNBH_2DMA)_2](PF_6)_2 \cdot THF$	2169.9	2153.5
$[Fe(phen)_2(CNBH_2 4\text{-}Pic)_2](PF_6)_2$	2166.4	2149.3
$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$	2164.9	2147.6
$[Fe(phen)_2(CN)(CNBH_2TMA)](PF_6)$		
$[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$	2148.2	2115.0
$[Fe(phen)_2(CNBBr_2TMA)_2](PF_6)_2$	2151.0	2111.6
$Fe(bipy)_2(CN)_2$	2082.3	2069.2
$[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	2169.4	2152.6
$[Fe(bipy)_2(CN)(CNBH_2DMA)](PF_6)$	2141.2	2087.2
$[Fe(bipy)_2(CNBH_2 4\text{-}Pic)_2](PF_6)_2$	2165.9	2148.6
$[Fe(bipy)_2(CNBH_2TMA)_2](PF_6)_2$	2164.8	2147.5
$Ru(bipy)_2(CN)_2$	2081.2	2059.4
$[Ru(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	2166.3	2139.0
$[Ru(bipy)_2(CNBH_2 4\text{-}Pic)_2](PF_6)_2$	2162.4	2134.4
$[Ru(bipy)_2(CN)(CNBH_2 4\text{-}Pic)](PF_6)$	2122.1	2082.8
$[Ru(bipy)_2(\underline{CN}BH_2TMA)_2](PF_6)_2$	2161.2	2133.3
$[Ru(bipy)_2(\underline{NC}BH_2TMA)_2](PF_6)_2$	2214.9 (weak)	

Table 6. B-H stretching frequencies of hexafluorophosphate salts in potassium chloride pellets (frequencies in cm^{-1}).

	ν_1	ν_2	ν_3	ν_4
$[Fe(phen)_2(CNBH_2DMA)_2](PF_6)_2 \cdot THF$	2427.1	2361.1	2336.5	2274.9
$[Fe(phen)_2(CNBH_2 4\text{-}Pic)_2](PF_6)_2$	2433.6	2363.1	------	2268.1
$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$	2431.7	2360.3	2296.9	2254.7
$[Fe(phen)_2(CN)(CNBH_2TMA)_2](PF_6)$				
$[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	2430.3	2360.7	2338.1	2272.0
$[Fe(bipy)_2(CN)(CNBH_2DMA)_2](PF_6)$	2422.9	------	2336.1	2271.6
$[Fe(bipy)_2(CNBH_2 4\text{-}Pic)_2](PF_6)_2$	2435.6	2363.8	------	2265.4
$[Fe(bipy)_2(CNBH_2TMA)_2](PF_6)_2$	2433.4	2360.4	2292.4	2248.6
$[Ru(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	2426.5	2362.5	2336.0	2272.3
$[Ru(bipy)_2(CNBH_2 4\text{-}Pic)_2](PF_6)_2$	2430.9	2362.2	------	2269.2
$[Ru(bipy)_2(CN)(CNBH_2 4\text{-}Pic)_2](PF_6)$	2424.0	2353.0	2279.6	2251.1
$[Ru(bipy)_2(\underline{CN}BH_2TMA)_2](PF_6)_2$	2433.3	2361.4	2292.3	2251.8
$[Ru(bipy)_2(\underline{NC}BH_2TMA)_2](PF_6)_2$	2418.4	2327.9	------	------

Table 7. Proton chemical shifts for selected hexafluorophosphate salts and related compounds in deuterated acetonitrile (chemical shifts in ppm).

	δ_A	δ_B	δ_C	δ_D	δ_E
1,10-phenanthroline (phen)	9.114	7.697	8.368	---	7.890
2,2'-bipyridine (bipy)	8.660	7.380	7.882	8.421	---
$[Fe(phen)_2(CNBH_2$4-Pic$)_2](PF_6)_2$	9.325	8.006	8.753	---	8.199
$[Fe(bipy)_2(CNBH_2$4-Pic$)_2](PF_6)_2$	8.936	7.611	8.164	8.337	---
$[Ru(bipy)_2(CNBH_2$4-Pic$)_2](PF_6)_2$	9.051	7.689	8.219	8.435	---
4-PicBH_3	---	---	---	---	---
$[Fe(phen)_2(CNBH_2DMA)_2](PF_6)_2$	9.473	8.091	8.797	---	8.237
$[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	9.094	7.739	8.244	8.458	---
$[Ru(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	9.125	7.766	8.249	8.488	---
$DMABH_3$	---	---	---	---	---
$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$	9.438	8.087	8.808	---	8.247
$[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$	9.351	8.144	8.877	---	8.276
$[Fe(bipy)_2(CNBH_2TMA)_2](PF_6)_2$	9.059	7.709	8.215	8.434	---
$[Ru(bipy)_2(\underline{CN}BH_2TMA)_2](PF_6)_2$	9.164	7.767	8.255	8.498	---
$[Ru(bipy)_2(\underline{NC}BH_2TMA)_2](PF_6)_2$	9.284	7.841	8.246	8.511	---
$TMABH_2NC$	---	---	---	---	---
$TMABH_2CN$	---	---	---	---	---
$TMABH_3$	---	---	---	---	---

*** These peaks were present but were not spin simulated and therefore were not reported.

Table 7 continued.

$\delta_{E'}$	$\delta_{D'}$	$\delta_{C'}$	$\delta_{B'}$	$\delta_{A'}$	δ_{Amines}		
7.890	---	8.368	7.697	9.114	---	---	---
---	8.421	7.881	7.380	8.660	---	---	---
					$\delta_{2,6}$	$\delta_{3,5}$	δ_{Me}
8.135	---	8.505	7.465	7.362	***	***	***
---	8.301	8.020	7.307	7.185	8.151	7.485	2.526
---	8.352	8.030	7.333	7.492	***	***	2.526
---	---	---	---	---	8.365	7.388	2.444
					δ_{Me}	$\delta_{Me'}$	δ_{NH}
8.170	---	8.539	7.507	7.434	2.160	2.152	5.263
---	8.414	8.090	7.391	7.299	2.270	2.242	4.965
---	8.401	8.053	7.367	7.561	2.269	2.249	4.951
---	---	---	---	---	2.386	2.386	4.434
					δ_{Me}		
8.186	---	8.563	7.530	7.477	2.258		
8.221	---	8.626	7.580	7.464	4 Peaks		
---	8.392	8.069	7.371	7.301	2.359		
---	8.411	8.064	7.377	7.586	2.390		
---	8.373	7.940	7.256	7.699	2.391		
---	---	---	---	---	2.597		
---	---	---	---	---	2.659		
---	---	---	---	---	2.574		

Table 8. Proton coupling constants for selected hexafluorophosphate complexes and related compounds in deuterated acetonitrile (shifts in ppm).

	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}
phen	4.31	1.78	---	8.10	---	---
bipy	4.79	1.81	0.94	7.52	1.22	8.01
$[Fe(phen)_2(CNBH_2$4-Pic$)_2](PF_6)_2$	5.25	1.24	---	8.28	---	---
$[Fe(bipy)_2(CNBH_2$4-Pic$)_2](PF_6)_2$	5.65	1.51	0.80	7.65	1.37	8.16
$[Ru(bipy)_2(CNBH_2$4-Pic$)_2](PF_6)_2$	5.61	1.55	0.80	7.70	1.37	8.30
4-PicBH_3	---	---	---	---	---	---
$[Fe(phen)_2(CNBH_2DMA)_2](PF_6)_2$	5.25	1.19	---	8.26	---	---
$[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	5.66	1.51	0.81	7.65	1.38	8.22
$[Ru(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	5.62	1.54	0.80	7.69	1.37	8.30
$DMABH_3$	---	---	---	---	---	---
$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$	5.22	1.26	---	8.31	---	---
$[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$	5.25	1.23	---	8.30	---	---
$[Fe(bipy)_2(CNBH_2TMA)_2](PF_6)_2$	5.66	1.50	0.80	7.64	1.38	8.19
$[Ru(bipy)_2(\underline{CN}BH_2TMA)_2](PF_6)_2$	5.61	1.53	0.84	7.71	1.34	8.25
$[Ru(bipy)_2(\underline{NC}BH_2TMA)_2](PF_6)_2$	5.59	1.53	0.81	7.67	1.33	8.28

Table 8. Extended.

$J_{EE'}$	$J_{A'B'}$	$J_{A'C'}$	$J_{A'D'}$	$J_{B'C'}$	$J_{B'D'}$	$J_{C'D'}$	J_{Amine}
---	4.31	1.78	---	8.10	---	---	---
---	4.79	1.81	0.94	7.52	1.22	8.01	---
8.92	5.19	1.28	---	8.25	---	---	$J_{23} = J_{56} = ****$ $J_{25} = J_{36} = ****$ $J_{Me-3} = J_{Me-5} = ****$
---	5.63	1.50	0.81	7.62	1.32	8.18	$J_{23} = J_{56} = ****$ $J_{25} = J_{36} = ****$ $J_{Me-3} = J_{Me-5} = ****$
---	5.51	1.57	0.83	7.66	1.25	8.29	$J_{23} = J_{56} = ****$ $J_{25} = J_{36} = ****$ $J_{Me-3} = J_{Me-5} = ****$
---	---	---	---	---	---	---	$J_{23} = J_{56} = 4.83$ $J_{25} = J_{36} = 1.80$ $J_{Me-3} = J_{Me-5} = 0.73$
8.97	5.21	1.25	---	8.25	---	---	$J_{Me\ -H} = 5.62$ $J_{Me'-H} = 5.61$
---	5.63	1.50	0.82	7.62	1.31	8.21	$J_{Me\ -H} = 5.64$ $J_{Me'-H} = 5.62$
---	5.51	1.57	0.83	7.67	1.26	8.30	$J_{Me\ -H} = 5.86$ $J_{Me'-H} = 5.85$
---	---	---	---	---	---	---	$J_{Me-H} = 5.62$
8.92	5.19	1.27	---	8.10	---	---	---
8.93	5.25	1.29	---	8.25	---	---	---
---	5.64	1.50	0.81	7.63	1.31	8.19	---
---	5.50	1.59	0.83	7.60	1.30	8.23	---
---	5.65	1.51	0.79	7.65	1.35	8.26	---

Table 9. Boron-11 chemical shifts for the hexafluorophosphate complexes and related compounds in deuterated acetonitrile (shifts in ppm).

	δ	Multiplicity
$TMABH_3$	-26.7	Quartet, J_{BH} = 97 Hz
$DMABH_3$	-32.4	Quartet, J_{BH} = 95 Hz
4-PicBH_3	-30.9	Quartet, J_{BH} = 97 Hz
$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$	-25.9	Broad Peak
$[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$	-17.8	Broad Peak
$[Fe(phen)_2(CNBBr_2TMA)_2](PF_6)_2$		Decomposition
$[Fe(phen)_2(CN)(CNBH_2TMA)](PF_6)$	-25.4	Broad Peak
$[Fe(phen)_2(CNBH_2DMA)_2](PF_6)_2$	-28.9	Broad Peak
$[Fe(phen)_2(CNBH_2 4\text{-Pic})_2](PF_6)_2$	-26.6	Broad Peak
$[Fe(bipy)_2(CNBH_2TMA)_2](PF_6)_2$	-23.1	Broad Peak
$[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	-27.1	Broad Peak
$[Fe(bipy)_2(CN)(CNBH_2DMA)](PF_6)$		
$[Fe(Bipy)_2(CNBH_2 4\text{-Pic})_2](PF_6)_2$	-24.7	Broad Peak
$[Ru(bipy)_2(\underline{CN}BH_2TMA)_2](PF_6)_2$	-26.5	Broad Peak
$[Ru(bipy)_2(\underline{NC}BH_2TMA)_2](PF_6)_2$	-32.6	Broad Peak
$[Ru(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	-29.7	Broad Peak
$[Ru(Bipy)_2(CNBH_2 4\text{-Pic})_2](PF_6)_2$	-27.9	Broad Peak
$[Ru(Bipy)_2(CN)(CNBH_2 4\text{-Pic})](PF_6)$		
$\underline{CN}BH_2TMA$	-26.6	Triplet, J_{BH} = 108 Hz
$\underline{NC}BH_2TMA$	-32.5	Triplet, J_{BH} = 103 Hz

$$M(diamine)_2(CN)_2 \longrightarrow [M(diamine)_2(CNBH_2amine)_2]^{+2} \quad \text{(Eq. 4)}$$
$$+ \qquad\qquad\qquad +$$
$$2\ amineBH_2I \qquad\qquad 2\ I^-$$

where the amine was trimethylamine (TMA), dimethylamine (DMA) or 4-picoline (4-Pic). Reactions between $Fe(phen)_2(CN)_2$ and amine-iodoboranes were slow; large scale reactions taking up to two days to complete. Reactions of amine-iodoboranes with $Fe(bipy)_2(CN)_2$ were more rapid than with the phenanthroline complexes. These reactions yielded iron complexes which varied in color from orange to red-orange. The yellow $[Ru(bipy)_2(CNBH_2amine)_2]I_2$ salts were prepared in a manner analogous to the iron salts but the reactions between the amine-iodoborane and $Ru(bipy)_2(CN)_2$ were more rapid than with the corresponding iron compound.

3.2.1.1 Syntheses of cis-bis(1,10-phenanthroline)bis(amine-isocyanoborane)iron(II) iodides; cis-$[Fe(phen)_2(CNBH_2TMA)_2]I_2$, cis-$[Fe(phen)_2(CNBH_2DMA)_2]I_2$, and cis-$[Fe(phen)_2(CNBH_24\text{-}Pic)_2]I_2$

These three complexes, cis-$[Fe(phen)_2(CNBH_2TMA)_2]I_2$, cis-$[Fe(phen)_2(CNBH_2DMA)_2]I_2$ and cis-$[Fe(phen)_2(CNBH_24\text{-}Pic)_2]I_2$, were prepared similarly and were isolated in overall yields of 89.0%, 61.4% and 83.9%, respectively. To illustrate the method, the synthesis of cis-$[Fe(phen)_2(CNBH_2TMA)_2]I_2$ is presented here.

A 0.546 g (2.15 mmol) sample of iodine was added with vigorous stirring to a solution of 0.312 g (4.28 mmol) of freshly sublimed trimethylamine-borane in 20 mL of methylene chloride in a 50 mL round-bottom flask. After the evolution

of H_2 ceased and the solution turned colorless, a 0.499 g (1.07 mmol) sample of cis-$Fe(phen)_2(CN)_2$ was added. After the neck and walls of the flask were again rinsed with 5 mL of solvent, the flask was stoppered and the contents stirred overnight. The resulting slightly turbid red-orange mixture was filtered into a 250 mL florence flask. The round-bottom flask was rinsed with an additional 5 mL of solvent and the rinse filtered into the florence flask. The crude CH_2Cl_2/CCl_4 solvated complex was precipitated by the slow, dropwise, addition of 120 mL of CCl_4 to the vigorously stirred filtrate. The orange solid was filtered, washed with 10 mL of CCl_4 and vacuum dried. The yield was 0.913 g.

The solvated complex was dissolved in 30 mL of acetonitrile and the resulting solution filtered into a 250 mL florence flask. The orange complex was precipitated overnight by the slow, dropwise, addition of 120 mL of diethyl ether to the vigorously stirred filtrate. The pure solid was filtered, rinsed with 10 mL of ether and dried under vacuum. The yield was 0.821 g (89.0% overall).

3.2.1.2 Syntheses of cis-bis(2,2'-bipyridine)bis(amine-isocyanoborane)iron(II) iodides; cis-$[Fe(bipy)_2(CNBH_2TMA)_2]I_2$, cis-$[Fe(bipy)_2(CNBH_2DMA)_2]I_2$, and cis-$[Fe(bipy)_2(CNBH_2$4-Pic$)_2]I_2$

The three complexes, cis-bis(2,2'-bipyridine)-bis(trimethylamine-isocyanoborane)iron(II) iodide, cis-bis(2,2'-bipyridine)bis(dimethylamine-isocyanoborane)-iron(II) iodide and cis-bis(2,2'-bipyridine)bis(4-picoline-isocyanoborane)iron(II) iodide, were prepared analogously

and isolated in final, overall yields of 94.8%, 87.4% and 94.2%, respectively. For brevity only the synthesis of cis-$[Fe(bipy)_2(CNBH_2TMA)_2]I_2$ is given.

A 0.658 g sample (9.02 mmol) of freshly sublimed trimethylamine-borane was dissolved in 25 mL of CH_2Cl_2 in a 50 mL round-bottom flask. Iodine (1.143 g, 9.01 mmol) was added in small portions to reduce effervescence. The neck and inside walls of the flask were rinsed with 10 mL of solvent. After the evolution of hydrogen ceased and the solution was colorless, 1.263 g (3.01 mmol) of cis-$Fe(bipy)_2(CN)_2$ were added and the neck and inside walls again rinsed with 5 mL of CH_2Cl_2. The flask was stoppered and the contents stirred overnight. The slightly turbid red mixture was filtered into a 250 mL florence flask and the round-bottom flask and filter were rinsed with 10 mL of solvent which was added to the filtrate. The crude solvated product was precipitated by the slow, dropwise, addition of 75 mL of CCl_4 overnight. The orange solid was filtered, rinsed with 10 mL of CCl_4 and dried under vacuum. The crude yield was 2.802 g.

The solid was purified by first dissolving the solvated complex in 30 mL of acetonitrile, then filtering the red solution into a 250 mL florence flask and finally reprecipitating the complex by the slow, dropwise, addition of 75 mL of diethyl ether overnight. The final orange product was filtered, washed with 25 mL ether and dried under vacuum. The final yield was 2.505 g (94.8% overall).

3.2.1.3 Syntheses of cis-bis(2,2'-bipyridine)bis(amine-isocyanoborane)ruthenium(II) iodides; cis-[Ru(bipy)$_2$(CNBH$_2$TMA)$_2$]I2, cis-[Ru(bipy)$_2$(CNBH$_2$DMA)$_2$]I$_2$, and cis-[Ru(bipy)$_2$(CNBH$_2$4-Pic)$_2$]I$_2$

Using similar procedures the complexes, cis-[Ru(bipy)$_2$(CNBH$_2$TMA)$_2$]I$_2$, cis-[Ru(bipy)$_2$(CNBH$_2$DMA)$_2$]I$_2$ and cis-[Ru(bipy)$_2$(CNBH$_2$4-Pic)$_2$]I$_2$, were synthesized and isolated in overall yields of 81.5%, 53.8% and 90.3%, respectively.

In a typical preparation, iodine (0.429, 1.69 mmol) was added (in small portions to lessen frothing caused by H_2 evolution) to a solution of freshly sublimed trimethylamine-borane (0.257 g, 3.52 mmol) dissolved in 20 mL of methylene chloride. When the evolution of H_2 ceased, 0.223 g of Ru(bipy)$_2$(CN)$_2$ (0.479 mmol) was added with stirring. The flask was stoppered and the contents stirred overnight. After filtering the yellow mixture, the filter was rinsed with 5 mL of CH_2Cl_2 and this rinse combined with the filtrate. The crude solvated product was precipitated by the addition of 120 mL of carbon tetrachloride overnight. This product was filtered, washed with 25 mL of CCl_4 and dried under vacuum. The yield was 0.429 g.

The pure iodide salt was obtained by first redissolving the solid in 15 mL of acetonitrile, filtering the mixture and rinsing the filter with 5 mL of solvent. The product was then precipitated by the dropwise addition of 120 mL of diethyl ether overnight. Finally, after filtering the

yellow solid, the product was rinsed with 50 mL of ether and dried under vacuum. The yield was 0.337 g (81.5% overall).

3.2.2 Characterization of Bis(amine-isocyanoborane) Iodide Complexes

These salts were soluble and stable in methylene chloride and acetonitrile. They dissolved in methanol but were slowly degraded, yielding the original cyano complexes. These solids picked up water rapidly upon exposure to the atmosphere and consequently it was difficult to get correct elemental analyses for the nonhydrated complexes. The elemental analyses for these hygroscopic solids are listed in Table 10. Occasionally, the elemental analyses indicated the presence of ether. The ether could be removed by redissolving the solid in acetonitrile, refluxing to drive off the more volatile ether and evaporating the mixture to dryness to recover the purified complex. If desired these complexes may be purified by chromatography on Sephadex LH-20 resin using acetonitrile as eluent.

3.2.3 Syntheses of Bis(amine-isocyanoborane) Hexafluorophosphate Complexes

Complexes with general formulas of $[Fe(phen)_2(CNBH_2amine)_2](PF_6)_2$ and $[M(bipy)_2(CNBH_2amine)_2](PF_6)_2$ (where M is Fe or Ru) were prepared by either metathesis of the iodide salts with silver hexafluorophosphate in acetonitrile or by precipitation from methanol/water solutions of the corresponding iodides by the addition of aqueous ammonium hexafluorophosphate solutions.

Table 10. Elemental analyses of the iodo complexes.

		%C	%H	%N
$[Fe(phen)_2(CNBH_2TMA)_2]I_2$	Calculated	44.38	4.42	12.94
	Found	44.38	4.63	12.80
$[Fe(phen)_2(CNBH_2DMA)_2]I_2$	Calculated	43.00	4.09	13.37
	Found	42.89	4.12	13.35
$[Fe(phen)_2(CNBH_2$4-Pic$)_2]I_2$	Calculated	48.87	3.67	12.00
	Found	49.07	3.65	11.86
$[Fe(bipy)_2(CNBH_2TMA)_2]I_2$	Calculated	41.12	4.68	13.70
	Found	40.94	4.67	13.44
$[Fe(bipy)_2(CNBH_2DMA)_2]I_2$	Calculated	39.54	4.34	14.19
	Found	39.58	4.38	14.42
$[Fe(bipy)_2(CNBH_2$4-Pic$)_2]I_2$	Calculated	46.09	3.87	12.65
	Found	45.83	3.77	12.36
$[Ru(bipy)_2(CNBH_2TMA)_2]I_2$	Calculated	38.96	4.44	12.98
	Found	38.61	4.41	13.17
$[Ru(bipy)_2(CNBH_2DMA)_2]I_2$	Calculated	37.39	4.10	13.42
	Found	37.32	4.05	13.69
$[Ru(bipy)_2(CNBH_2$4-Pic$)_2]I_2 \cdot \frac{1}{2}H_2O$	Calculated	43.43	3.75	11.92
	Found	43.36	3.68	11.94

3.2.3.1 Syntheses of cis-bis(1,10-phenanthroline)bis(amine-isocyanoborane)iron(II) hexafluorophosphates; cis-$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$, cis-$[Fe(phen)_2(CNBH_2DMA)_2](PF_6)_2$, and cis-$[Fe(phen)_2(CNBH_2$4-Pic$)_2](PF_6)_2$

Using similar procedures, the three complexes cis-$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$, cis-$[Fe(phen)_2(CNBH_2DMA)_2]$-$(PF_6)_2$ and cis-$[Fe(phen)_2(CNBH_2$4-Pic$)_2](PF_6)_2$, were prepared in yields of 78.8%, 57.8% and 81.9%, respectively. For concision, only the synthesis of the trimethylamine complex is provided.

Cis-$[Fe(phen)_2(CNBH_2TMA)_2]I_2$ (0.694 g, 0.801 mmol) was dissolved in 25 mL of acetonitrile in a 50 mL round-bottom flask. Silver hexafluorophosphate (0.498 g, 1.97 mmol) was added and any residue on the neck and inside walls of the flask was rinsed into the flask with 5 mL of additional solvent. The flask was stoppered and the contents stirred overnight. The precipitated AgI was filtered and rinsed with 10 mL of acetonitrile. This rinse was added to the filtrate and the crude product was precipitated by the slow dropwise addition of 60 mL of diethyl ether. The orange powder was filtered, washed with 50 mL of ether and dried under vacuum to yield 0.64 g.

The purified product was obtained by first redissolving the solid in 10 mL of acetonitrile. Following filtration to remove any undissolved solids the filter was rinsed with 5 mL of additional solvent and the complex reprecipitated by the addition of 60 mL of ether. The purified product was filtered, rinsed with 50 mL of ether and dried under vacuum.

The yield was 0.570 g (78.8%). This complex can also be prepared by precipitation from water/methanol solutions of the iodide complex by the addition of aqueous NH_4PF_6. The product can be recrystallized from methanol/acetonitrile mixtures in good yield.

3.2.3.2 Syntheses of cis-bis(2,2'-bipyridine)bis(amine-isocyanoborane)iron(II) hexafluorophosphates; cis-$[Fe(bipy)_2(CNBH_2TMA)_2](PF_6)_2$, cis-$[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$, and cis-$[Fe(bipy)_2(CNBH_2$4-Pic$)_2](PF_6)_2$

Employing similar procedures, the three complexes, cis-$[Fe(bipy)_2(CNBH_2TMA)_2](PF_6)_2$, cis-$[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$ and cis-$[Fe(bipy)_2(CNBH_2$4-Pic$)_2](PF_6)_2$, were prepared in yields of 96.5%, 72.5% and 91.5%, respectively. In the interest of tersicity, only the synthesis of the trimethylamine complex is given.

A 1.661 g (2.030 mmol) sample of cis-$[Fe(bipy)_2(CNBH_2TMA)_2]I_2$ was dissolved in a mixture of 30 mL of water and 30 mL of methanol. The crude PF_6^- salt was precipitated by the slow addition of 6.0 g (36.8 mmol) of NH_4PF_6 in 30 mL of water. To complete the precipitation, an additional 40 mL of water were slowly added. The solid was filtered and washed first with 100 mL of H_2O and then with 30 mL of diethyl ether. After drying overnight under vacuum, the yield was 1.720 g.

The product was purified by first dissolving the crude material in 25 mL of acetonitrile and filtering the mixture to remove any undissolved solids. The filter was then

washed with 5 mL of solvent and this was added to the filtrate. One hundred and fifty mL of ether were added dropwise to the filtrate to cause precipitation of the title complex. Finally, after the addition of ether was completed, the product was filtered, washed with 50 mL diethyl ether and dried under vacuum overnight. The yield was 1.673 g or 96.5%. If necessary, this solid may be recrystallized from acetonitrile/methanol mixtures in good yield.

3.2.3.3 Syntheses of cis-bis(2,2'-bipyridine)bis(amine-isocyanoborane)ruthenium(II) hexafluorophosphates; cis-$[Ru(bipy)_2(CNBH_2TMA)_2](PF_6)_2$, cis-$[Ru(bipy)_2(CNBH_2DMA)_2](PF_6)_2$, and cis-$[Ru(bipy)_2(CNBH_2$4-Pic$)_2](PF_6)_2$

These complexes, cis-$[Ru(bipy)_2(CNBH_2TMA)_2](PF_6)_2$, cis-$[Ru(bipy)_2(CNBH_2DMA)_2](PF_6)_2$ and cis-$[Ru(bipy)_2(CNBH_2$-4-Pic$)_2](PF_6)_2$, were prepared analogously in yields of 88.5%, 88.5% and 72.5%, respectively.

In a typical preparation a 1.564 g (1.811 mmol) sample of cis-$[Ru(bipy)_2(CNBH_2TMA)_2]I_2$ was dissolved in a mixture of 20 mL of methanol and 10 mL of water. The crude PF_6^- salt was precipitated by the slow addition of ammonium hexafluorophosphate (6.25 g, 38.3 mmol) in 25 mL of water. The precipitation was completed by the addition of 20 mL of water. Following filtration, the yellow solid was washed first with 50 mL of water, then with 50 mL of diethyl ether and finally dried under vacuum. The yield was 1.549 g.

The compound was purified by heating the solid in a mixture of 15 mL of tetrahydrofuran and 8 mL of acetonitrile to reflux, filtering to remove any undissolved solids and setting the mixture aside to cool overnight. The yellow crystals were filtered, rinsed with 10 mL of THF and dried under vacuum to yield a first crop of 0.678 g. The filtrate was evaporated to dryness and the solid recrystallized from 10 mL of a 1:1 THF/CH_3CN mixture. After filtering and rinsing with 10 mL of THF, the second crop was dried under vacuum. Finally, 30 mL of diethyl ether were added to the filtrate to complete precipitation. The final crop was filtered, rinsed with 10 mL of diethyl ether and dried. The elemental analysis of the yellow crystals indicated the presence of tetrahydrofuran. A ^1H NMR spectrum run on a sample of the yellow crystals in acetonitrile confirmed the presence of THF. The solvate was broken by dissolving the combined yields in 15 mL of acetonitrile, refluxing the mixture to remove the more volatile THF and finally, reprecipitating the solid by the dropwise addition of 75 mL of diethyl ether. This product was filtered, rinsed with 10 mL of ether and dried under vacuum. The final yield was 1.441 g or 88.5% overall.

3.2.4 Characterization of Bis(amine-isocyanoborane) Hexafluorophosphate Complexes

These complexes are only sparingly soluble in water, methanol, THF, and diethyl ether. They are soluble in

methylene chloride and acetonitrile. Like their corresponding iodide salts, these solids are decomposed by prolonged exposure to methanol or water. The PF_6^- salts are also hygroscopic but much less so than the iodides. Samples of all the solids which were kept in a dry-box showed no water in the ^1H NMR with deuterated acetonitrile as solvent. The elemental analyses for the hexafluorophosphate salts are listed in Table 11. Water was detected in the IR spectra of all of the complexes which were exposed to the atmosphere for any length of time. The individual IR spectra are shown in Appendix A while the C≡N and B-H stretching frequencies for these complexes are listed in Tables 5 and 6, respectively. These complexes were also analyzed using proton and ^{11}B NMR spectroscopy. The ^1H chemical shifts and coupling constants obtained for the complexes in deuterated acetonitrile solutions are listed in Tables 7 and 8, respectively. Table 9 contains the ^{11}B chemical shifts for these hexafluorophosphate complexes measured at 96 MHz. All of the complexes were further characterized by cyclic voltammetry and UV-VIS spectroscopy. The $Fe^{+3/+2}$ and $Ru^{+3/+2}$ $E_{\frac{1}{2}}$ values, obtained from the cyclic voltammograms of these salts in acetonitrile solutions are, listed in Table 4. Table 1 lists the λ_{max} in the UV-VIS spectrum (Appendix B).

Table 11. Elemental analyses of the hexafluorophosphate complexes.

		%C	%H	%N
$[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$	Calcd	36.96	3.30	10.78
	Found	36.96	3.38	10.56
$[Fe(phen)_2(CN)(CNBH_2TMA)](PF_6)\cdot H_2O\cdot MeOH$	Calcd	49.14	4.54	13.37
	Found	48.89	4.36	13.30
$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$	Calcd	42.61	4.25	12.42
	Found	42.41	4.23	12.25
$[Fe(phen)_2(CNBH_2DMA)_2](PF_6)_2\cdot THF$	Calcd	43.16	4.47	11.84
	Found	43.09	4.48	11.78
$[Fe(phen)_2(CNBH_24\text{-}Pic)_2](PF_6)_2$	Calcd	47.05	3.53	11.55
	Found	46.75	3.42	11.31
$[Fe(bipy)_2(CN)(CNBH_2DMA)](PF_6)\cdot 2H_2O$	Calcd	43.73	4.43	14.87
	Found	43.58	4.18	14.75
$[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$	Calcd	37.81	4.15	13.57
	Found	37.78	4.09	13.36
$[Fe(bipy)_2(CNBH_2TMA)_2](PF_6)_2$	Calcd	39.38	4.48	13.12
	Found	39.14	4.34	12.88
$[Fe(bipy)_2(CNBH_24\text{-}Pic)_2](PF_6)_2$	Calcd	44.29	3.72	12.15
	Found	44.19	3.74	12.13

Table 11. Continued.

$[Ru(bipy)_2(CN)(CNBH_2 4\text{-Pic})](PF_6)\cdot H_2O$	Calcd	46.36	3.61	13.52
	Found	46.38	3.62	13.52
$[Ru(bipy)_2(CNBH_2 4\text{-Pic})_2](PF_6)_2$	Calcd	42.22	3.54	11.58
	Found	41.91	3.46	11.37
$[Ru(bipy)_2(CNBH_2 TMA)_2](PF_6)_2$	Calcd	37.40	4.26	12.46
	Found	37.30	4.01	12.36
$[Ru(bipy)_2(CNBH_2 DMA)_2](PF_6)_2$	Calcd	35.84	3.93	12.86
	Found	35.63	3.62	12.54

3.3 Syntheses and Characterization of Derivatives

3.3.1 Syntheses of Bis(trimethylamine-dihaloisocyanoborane) bis(1,10-phenanthroline)iron(II) Hexafluorophosphate Complexes

Bis(amine-haloisocyanoborane) hexafluorophosphate complexes were prepared by direct halogen oxidation of cis-$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$ in methylene chloride solution using chlorine and bromine.

3.3.1.1 Synthesis of cis-bis(trimethylamine-dichloro-isocyanoborane)bis(1,10-phenanthroline)iron(II) hexafluorophosphate, cis-$[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$

Chlorine gas was bubbled through 9 mL of CH_2Cl_2 containing 0.2775 g (0.3076 mmol) of cis-$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$. At the end of two hours the addition of chlorine was halted and the solvent was removed by passing a stream of gaseous nitrogen through the flask. Any remaining traces of volatile materials were removed by drying the solid under vacuum for thirty minutes. The yield of the crude material was 0.3145 g.

The material was initially purified by dissolving the solid in a hot mixture of 15 mL of water and 2 mL of methanol. A pea-sized portion of NH_4PF_6 was added to the hot solution and the mixture set aside to cool. The yellow crystals were filtered, washed with 5 mL of water and 5 mL of methanol, and air dried.

Final purification was achieved by heating the solid in 40 mL of methanol to which enough acetonitrile was added to

effect dissolution. Following crystallization, the solid was filtered, washed with 5 mL of methanol and dried under vacuum. The yield was 0.2175 g (68.0%).

3.3.1.2 Characterization of cis-bis(trimethylamine-dichloroisocyanoborane)bis(1,10-phenanthroline)iron(II) hexafluorophosphate, cis-$[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$

The complex, $[Fe(phen)_2(BCl_2TMA)_2](PF_6)_2$, was remarkably stable towards solvolysis including hot methanol and acetonitrile as evidenced by its recrystallization from this mixture. It showed no evidence of decomposition even when exposed to the atmosphere for extended periods. The complex is soluble in methylene chloride and more so in acetonitrile. The elemental analysis for this complex is listed in Table 11. The C≡N stretching frequencies in the infrared spectrum of this compound are listed in Table 5. The ^1H NMR chemical shifts and coupling constants are listed in Tables 7 and 8, respectively. The UV-VIS, and cyclic voltammetry data for this compound are listed in Tables 1 and 4, respectively. The complete IR and UV-VIS spectra are shown in Appendices A and B, respectively.

3.3.1.3 Bromination of cis-bis(trimethylamine-isocyanoborane)bis(1,10-phenanthroline)iron(II) hexafluorophosphate, cis-$[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$

A 0.2603 g (0.2885 mmol) sample of $[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$ was placed in a fifty mL round-bottom flask in a well-ventilated hood. Five mL of liquid bromine were carefully poured into the flask in small

increments to avoid excessive frothing. The mixture was stirred for one hour under a stream of nitrogen gas during which time most of the excess bromine vaporized out of the flask. The residue was stirred with five mL of methylene chloride and the volatiles removed under a stream of nitrogen gas. An additional five mL of CH_2Cl_2 were added and the mixture rotary evaporated to dryness. The yield was 0.3671 g of yellow powder which still retained a faint odor of bromine.

Two attempts were made at purifying this solid. First, a 0.1465 g sample was dissolved in five mL of acetonitrile. Two mL of 1-hexene were added to remove any unreacted bromine. This mixture was stirred for five minutes and then rotary evaporated to dryness. Five mL of acetonitrile were added and the resulting mixture filtered to remove a slight bit of undissolved solid. The filtrate was chromatographed on Sephadex LH-20 resin with acetonitrile as eluent. The small faint yellow leading band was discarded and the broad, yellow trailing band was collected in two portions. The trailing edge of this band was significantly darker than the leading edge and was discarded. The remaining portion was rotary evaporated to dryness with a yield of 0.0295 g. The proton decoupled ^{11}B NMR of this sample contained three resonances instead of one expected for a single compound indicating the presence of three different boron containing products. One resonance was near that of the starting material, $[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$ and the other two

downfield in the direction expected for the possible products $[Fe(phen)_2(CNBBr_2TMA)_2](PF_6)_2$ and $[Fe(phen)_2(CNBHBrTMA)_2](PF_6)_2$. The elemental analysis of this sample (38.06% C, 3.78% H, 11.04% N) was consistent with a mixture of these products, since the calculated elemental analyses for the monobrominated product, $[Fe(phen)_2(CNBHBrTMA)_2](PF_6)_2$, is 36.26% C, 3.42% H, 10.57% N and for the dibrominated product, $[Fe(phen)_2(CNBBr_2TMA)_2](PF_6)_2$, is 31.56% C, 2.81% H, 9.20% N.

For the second attempt at purification, a 0.0920 g sample was dissolved in two mL of acetonitrile and a product reprecipitated by the addition of a large excess (approximately ten mL) of a saturated aqueous solution of NH_4PF_6. The precipitation was aided by an additional forty mL of water. The solid was filtered, washed first with water then with one mL of methanol to aid in drying. After drying overnight under vacuum, the yield was 0.0718 g. A sample was chromatographed on Sephadex LH-20 using acetonitrile as eluent with the center of the broad yellow band collected. A yellow solid was isolated by evaporation of the solvent. The elemental analysis for this solid was 35.06% C, 3.14% H, and 9.94% N, again indicating a mixture of products. No further attempts at purification were made.

This mixture was only partially characterized. The infrared spectrum was obtained from a small sample taken from the leading edge of the chromatographed sample but after the solvent was removed under vacuum. The infrared

spectrum (shown in Appendix B) has no significant stretches in the B-H stretching region from 2200-2400 cm^{-1} The C≡N stretching frequencies are listed in Table 5. The data imply the existence of a single compound, believed to be $[Fe(phen)_2(CNBBr_2TMA)_2](PF_6)_2$. The UV-VIS spectrum was obtained on a sample taken from the leading edge of the yellow band of a chromatographed sample. The wavelength of maximum absorbance is listed in Table 1 while the entire spectrum is listed in Appendix A.

3.3.2 Syntheses of cis-(cyano)(amine-isocyanoborane) Complexes

The syntheses of complexes; cis-(cyano)(trimethylamine-isocyanoborane)bis(1,10-phenanthroline)iron(II) hexafluorophosphate, $cis-[Fe(phen)_2(CN)(CNBH_2TMA)](PF_6)$; cis-(cyano)-(dimethylamine-isocyanoborane)bis(2,2'-bipyridine)iron(II) hexafluorophosphate, $cis-[Fe(bipy)_2(CN)(CNBH_2DMA)](PF_6)$; and cis-(cyano)(4-picoline-isocyanoborane)bis(2,2'-bipyridine)-ruthenium(II) hexafluorophosphate, $cis-[Ru(bipy)_2(CN)-(CNBH_24\text{-}Pic)](PF_6)$, were accomplished by the solvolysis of an amine borane group from a coordinated amine isocyanoborane ligand of the respective bis(amine-isocyanoborane) complexes using methanol as the solvent. This procedure was found to be more practical than the syntheses from amine-iodoboranes and the appropriate cyano complexes.

3.3.2.1 Synthesis of cis-(cyano)(trimethylamine-isocyanoborane)bis(1,10-phenanthroline)iron(II) hexafluorophosphate, cis-$[Fe(phen)_2(CN)(CNBH_2TMA)](PF_6)$

A sample of 0.2560 g (0.2838 mmol) of $[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$ and 25 mL of methanol were refluxed in a 50 mL round-bottom flask for 24 hours. The mixture was allowed to cool to room temperature and filtered to remove a small amount of blue-black solid $[Fe(phen)_2(CN)_2]$. The filtrate was reduced in volume to about 10 mL by rotary evaporation of the solvent. The sample was chromatographed on Sephadex LH-20 resin using methanol as the eluent. Three partially resolved bands were found to be present; a leading yellow band ($[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$), a red band ($[Fe(phen)_2(CN)(CNBH_2TMA)](PF_6)$), and a purple band $[Fe(phen)_2(CN)_2]$. The red portion was collected using a fraction collector and the solvent reduced to 4 mL by evaporation. This fraction was rechromatographed, again collecting only the center red portion. After removal of the solvent and drying under vacuum, the yield was 0.0550 g or 28.3% overall yield.

3.3.2.2 Synthesis of cis-(cyano)(dimethylamine-isocyanoborane)bis(2,2'-bipyridine)iron(II) hexafluorophosphate, cis-$[Fe(bipy)_2(CN)(CNBH_2DMA)](PF_6)$

A mixture of 20 mL of methanol and 0.1180 g (0.1429 mmol) of $[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$ were brought rapidly to reflux, whereupon the color of the mixture changed rapidly from a red to purple. The mixture was quickly cooled in a ice bath to room temperature and the methanol removed by

rotary evaporation. The residue was dissolved in a minimum of acetonitrile and the sample chromatographed on Sephadex LH-20 resin using acetonitrile as eluent. The sample separated into a red band and a slower moving purple band of $Fe(bipy)_2(CN)_2$. The red band was collected, the volume reduced by evaporation and the sample rechromatographed. Again the red portion was collected. After removal of the solvent and vacuum drying, the yield was 0.0535 g or 60.1% overall.

3.3.2.3 Synthesis of cis-(cyano)(4-picoline-isocyanoborane)-bis(2,2'-bipyridine)ruthenium(II) hexafluorophosphate, cis-$[Ru(bipy)_2(CN)(CNBH_24\text{-}Pic)](PF_6)$

The complex, cis-$[Ru(bipy)_2(CN)(CNBH_24\text{-}Pic)](PF_6)$, was synthesized by refluxing a mixture of 10 mL of methanol and 0.2285 g (0.2362 mmol) of $[Ru(bipy)_2(CNBH_24\text{-}Pic)_2](PF_6)_2$ for 50 minutes. After reduction of the volume by evaporation, the mixture was chromatographed on Sephadex LH-20 using acetonitrile as the eluent. The sample eluted as an amber band trailing into a red band $[Ru(bipy)_2(CN)_2]$. The amber band was collected, the solvent removed under a stream of nitrogen and the residue rechromatographed. Again the amber band was collected and the solvent removed (to dryness) by evaporation under vacuum. The yield after vacuum drying was 0.0630 g or 37.2% overall.

3.3.2.4 Characterization of cis-(cyano)(amine-isocyanoborane) Complexes

As expected, these compounds have physical properties between those of the bis(amine-isocyanoborane) complexes and the di(cyano) complexes. They are more soluble in polar solvents than the di(cyano) compounds but less soluble than the bis(amine-isocyanoborane) complexes. They are intermediate in color also. The complexes, cis-(cyano)-(trimethylamine-isocyanoborane)bis(1,10-phenanthroline)-iron(II) hexafluorophosphate and cis-(cyano)(dimethylamine-isocyanoborane)bis(2,2'-bipyridine)iron(II) hexafluorophosphate, are red. The ruthenium complex, cis-(cyano)-(4-picoline-isocyanoborane)-bis(2,2'-bipyridine)-ruthenium(II) hexafluorophosphate, is yellow-orange. The UV-VIS and infrared spectroscopic data are listed in Tables 1, 5 and 6, while the individual spectra are shown in Appendices A and B. The elemental analyses for these complexes are listed in Table 11 and the electrochemical data are listed in Table 4.

The cyano(amine-isocyanoborane) complexes were also characterized by ^{1}H NMR. The NMR's of these compounds are very complex. The ^{1}H NMR aromatic region of cis-(cyano)-(trimethylamine-isocyanoborane)bis(1,10-phenanthroline)-iron(II) hexafluorophosphate contains 64 resonances assignable to 16 different protons. There are more than 125 resonances assignable to the 16 aromatic ligand protons in the region between 7 and 10 ppm in the ^{1}H NMR's of cis-(cyano)-

(dimethylamine-isocyanoborane)bis(2,2'-bipyridine)iron(II) hexafluorophosphate and cis-(cyano)(4-methylpyridine-isocyanoborane)bis(2,2'-bipyridine)ruthenium(II) hexafluorophosphate. The resonances overlap, thus making detailed assignments impossible. Consequently, the chemical shifts and coupling constants for these complexes are not listed in Tables 7 and 8.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Structure Determination

Before considering the comparative behaviors of the reported isocyanide complexes some preliminary discussion of the complexes in general is appropriate. Elemental analysis provides information on the formulation and purity of a given complex. Tables 5 and 6 list this information for the new complexes reported here and show that the majority were isolated in high purity. However, elemental analysis provides no structural information on metal complexes regarding either the configuration about the metal center (i.e. geometric isomerization) or the possible existence of linkage isomers involving the cyanide ion. As the reported complexes have octahedral geometries around the metal ion and contain cyanide moieties, both types of isomerism must be considered before structure assignment can be made.

When dealing with any but the simplest of octahedral metal complexes, there exists the chance that a complex has more than a single geometric isomer. For any octahedral complex employing two symmetric bidentate ligands such as 2,2'-bipyridine or 1,10-phenanthroline, cis and trans

isomers are possible which ideally would give C_2 and D_{2h} symmetries, respectively (see Figures 4 and 5).

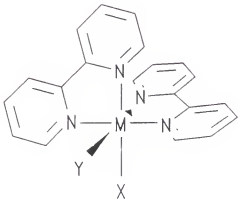

Figure 4. Cis isomer.

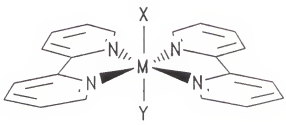

Figure 5. Trans isomer.

For many years the prevailing notion was that six coordinate bis-2,2'-bipyridine and bis-1,10-phenanthroline complexes could exist only in the cis geometry.[62] The rationale being that there would be severe steric strain between α H atoms on the ligands if in the trans (D_{2h}) geometry. This notion was supported by the lack of any examples of such trans complexes. Over the past twenty years, however, several trans complexes have been synthesized and their structures confirmed by X-ray crystallography. These include the eight coordinate complexes[63] $[Sr(phen)_2(OH)_4](ClO_4)_2 \cdot 2phen$ and $[Ba(phen)_2(OH)_4](ClO_4)_2 \cdot 2phen$, several square planar complexes of Ag, Cu, Hg, Pd, and Pt[64-73], as well as a growing number of octahedral complexes of Ru, and Os.[74-76]

Their structures confirm that the steric requirements of 2,2'-bipyridine and 1,10-phenanthroline are such that a planar arrangement (D_{2h}) of two such ligands about a given metal involving normal metal-to-nitrogen bonds would indeed produce an impossibly close approach of the α H atoms on opposite ligands.[62] The strain is relieved by either a tetragonal or rectangular distortion of the MN_4 skeleton, i.e., by a twisting or bowing of the ligand (see Figures 6 and 7). These distortions produce a bis-2,2'-bipyridine or bis-1,10-phenanthroline complex with D_2 symmetry when the ligands, X and Y, are identical or C_2 symmetry if they are not identical.

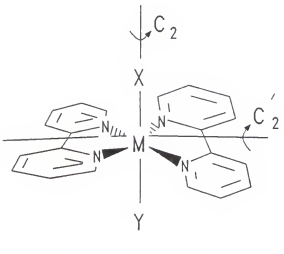

Figure 6. Ligand twist.

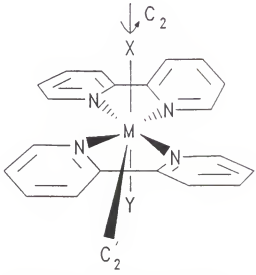

Figure 7. Ligand bowing.

When the two monodentate ligands are cis to each other, the resulting complex must have C_2 symmetry when X and Y are alike and C_1 symmetry when X and Y are dissimilar.

Without X-ray diffraction data, the geometries of complexes must be inferred from spectroscopic measurements. While a variety of techniques including IR, UV-VIS, and NMR spectroscopies can be used, the geometry is perhaps most effectively demonstrated by ^1H NMR. The number of distinct resonances found in the proton NMR of any octahedral bis-2,2'-bipyridine or bis-1,10-phenanthroline complex depends on the symmetry exhibited by that complex.

When the ligands X and Y are identical the trans complex will have D_2 symmetry if distortions are present or D_{2h} symmetry if no distortions occur. The cis complex will have C_2 symmetry. The presence of the principal C_2 axis in both geometries, cis (C_2 symmetry) and trans (either D_{2h} or D_2 symmetry), results in magnetic equivalence for the two bidentate ligands. However, in the trans geometries the presence of a C_2' axis bisecting the two ligands guarantees the magnetic equivalence of the two halves of any 2,2'-bipyridine or 1,10-phenanthroline. The absence of a second C_2 symmetry element in the cis geometry means the two halves of the 2,2'-bipyridine or 1,10-phenanthroline ligands are nonequivalent. Thus, for any bis-2,2'-bipyridine or bis-1,10-phenanthroline complex with trans configuration the eight ligand protons on either a 2,2'-bipyridine or a 1,10-phenanthroline will appear as only four separate resonances in the aromatic region of their ^1H NMR. In Figure 8 these resonances are assigned to A,A'; B,B'; C,C'; AND D,D'. Such a pattern is observed[77] in the ^1H NMR spectrum of the square

planar complex bis(2,2'-bipyridine)platinum(II) nitrate, $[Pt(bipy)_2](NO_3)_2$, in deuterated water. Perhaps a more appropriate example[78] is the octahedral complex trans-bis(oxo)bis(2,2'-bipyridine)osmium(VI) perchlorate, trans-$[Os(O)_2(bipy)_2](ClO_4)_2$, which exhibits this pattern in its ^1H NMR spectrum in deuterated dimethyl sulfoxide. It should be noted that both the cis and trans isomers of the later complex have been reported.[76]

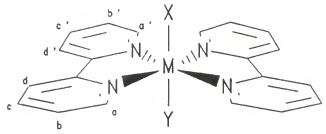

Figure 8. Labeling scheme for trans isomer.

The nonequivalence of the two ligand halves in a cis complexes (with C_2 symmetry) will produce eight different aromatic resonances in the proton NMR due to protons; A, B, C, D, A', B', C', AND D' in Figure 9. Obvious examples of complexes exhibiting this pattern are; the cis isomer of bis(oxo)bis(2,2'-bipyridine)osmium(VI) perchlorate,[76] cis-$[Os(O)_2(bipy)_2](ClO_4)_2$, the cis complex[78] of dicyanobis(1,10-phenanthroline)iron(II), cis-$Fe(phen)_2(CN)_2$, (a reference and starting material used in this study),and the diprotonated ion,[79] cis-$Fe(phen)_2(CNH)_2^{+2}$.

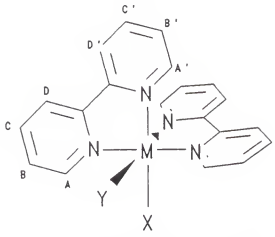

Figure 9. Labeling scheme for cis isomer.

Similarly, for bis-2,2'-bipyridine or bis-1,10-phenanthroline complex where the remaining ligands X and Y are nonequivalent, the cis and trans isomers again produce different numbers of resonances in their respective NMR spectra. In the absence of distortions the trans isomer would now have C_{2v}. Here, the principal C_2 axis would produce magnetic equivalence between the two bidentate ligands while the σ_v symmetry element would produce magnetic equivalence for the two halves of the ligands. Thus such a complex would again have only four resonances in the ^1H NMR spectrum. In a trans isomer with C_2 symmetry (i.e., a trans complex where ligand twisting occurs and where any isomerization/equilibration between the enantiomers is slow on the NMR time scale) the two bidentate ligands are again identical but the absence of a secondary C_2 axes would produce ligands with nonequivalent halves and therefore eight lines are found in the ^1H NMR of these complexes.

Such a pattern is observed in the ^1H NMR spectrum of the C_2 symmetric ion, $[Pt(bipy)_2(OH)]^+$, in alkaline D_2O solution.[77]

For a cis isomer (with C_1 symmetry) where X and Y are nonequivalent, the lack of any rotation axis or plane of symmetry causes the now nonequivalent and nonsymmetric 2,2'-bipyridine and 1,10-phenanthroline ligands to produce sixteen different resonances in the ^1H NMR.

Thus, the geometries of octahedral bis-2,2'-bipyridine or bis-1,10-phenanthroline complexes can be inferred from the number of distinct resonances in their ^1H NMR spectra. For complexes in which the remaining ligands, X and Y, are identical, the cis isomer would have eight proton resonances while the trans isomer would contain only four. If the ligand X and Y are not identical, the trans isomer would show a maximum of eight resonances in its ^1H NMR spectra compared to sixteen resonances for the cis isomer.

Table 7 lists the ^1H NMR resonances in deuterated acetonitrile of the hexafluorophosphate salts of the amine-isocyanoborane complexes and related compounds prepared in this study. All the metal complexes in which X = Y [i.e., bis(amine-cyanoborane) and bis(amine-isocyanoborane) complexes] have proton NMRs with eight resonances assignable to the 2,2'-bipyridines or 1,10-phenanthrolines, while the complexes in which X ≠ Y [i.e., cyano(amine-isocyanoborane) complexes] produce proton NMRs with sixteen separate resonances. Thus, all the complexes produced in this study have cis geometries.

Infrared spectroscopy has also been used[80] to differentiate cis and trans isomers particularly of bis cyano complexes. Structural assignment using IR spectroscopy is not always as clear cut as ^{1}H NMR, however. Here, the distinction is made on the basis of the number of C≡N stretches in the infrared spectrum of the complex. If two cyanides are present then two possible modes of CN stretch are possible; the symmetric stretch (see Figure 10), where the two nitrogen move synchronously about the two carbons and the asymmetric stretch, as shown in Figure 11, where the two nitrogens move asynchronously about the carbon atoms.

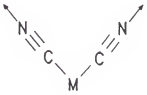

Figure 10. $M(CN)_2$ symmetric stretch.

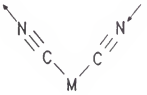

Figure 11. $M(CN)_2$ asymmetric stretch.

For any vibration (stretch) to be IR active (i.e., appear in the IR spectrum) that vibration must produce a change in the dipole moment of the species. For the trans isomer (see Figure 5), if both X and Y are identical CN-containing ligands, then the symmetric stretch of the two C≡N moieties produces no change in the dipole moment while the asymmetric stretch does produce a dipole moment change. Therefore, only the asymmetric stretch is IR active.

Similar inspection of Figure 4 reveals that for the cis isomer, when X and Y are identical C≡N-containing ligands, both the symmetric and asymmetric stretches produce a change in the dipole moment and therefore, both stretches are IR active. Thus, in the case of an octahedral bis-bidentate complex with two identical C≡N-containing ligands, the trans isomer should have only a single C≡N stretch present in the IR spectrum while the cis isomer should exhibit two such stretches.

The assignment of structure on the basis of IR spectroscopy can be hazardous. On occasion the symmetric and asymmetric stretches of a cis dicyano complex may be unresolvable and thus appear as only a single broad absorption. This might lead one to conclude erroneously that a complex is a trans isomer. Such is the case with cis dicyanobis(1,10-phenanthroline)iron(II).[81] When this material is recrystallized from chloroform the IR spectrum of the resulting solid contains only one C≡N at 2066 cm^{-1}. When this material is recrystallized from an aqueous solution it exhibits stretches at 2075 and 2062 cm^{-1}. Table 5 lists this complex in the anhydrous form with absorbances at 2080 and 2065 cm^{-1}. Thus if only a single absorption is present in the C≡N stretching region of the IR spectrum, the assignment of the trans structure may be premature as the complex may prove to be a cis isomer with the asymmetric and symmetric stretches unresolved. However, the definitive assignment of a cis structure is still possible, since if two C≡N absorptions are observed the complex must be the cis isomer.

Table 5 lists the C≡N stretching frequencies for the bis-amine isocyanoborane complexes in methylene chloride solutions. All of these complexes have two absorptions in the C≡N region, confirming their structures as the cis isomers.

The remaining difficulties in the structural assignments lie in the bonding arrangement about the CN moiety. It has been suggested[13] that transition metal complexes do not contain free N-bonded CN^- ligands because of a low barrier to isomerization from the N-bonded form to the more thermodynamically stable C-bonded form. However, when the CN^- ion is bonded simultaneously to two centers (i.e., μ-CN) the relative thermodynamic stability of the two isomers (M-C≡N-R vs. M-N≡C-R) is unclear. Under conditions of kinetic control, the reaction of a Lewis acid with a cyanide complex will lead to the formation of an isocyanide ligand.

$$\text{M-CN} \xrightarrow{+\ \text{Lewis acid}} \underset{\text{(isocyanide ligand)}}{\text{M-(CN-Acid)}}$$

Should a kinetically viable pathway exist there is the possibility of isomerization about the CN moiety either before Lewis acid-base adduct formation or after complexation.

$$\begin{array}{ccccc} \text{M-CN} & \xrightarrow{\text{isomerization}} & \text{M-NC} & \xrightarrow{+\ \text{Lewis acid}} & \underset{\text{(cyanide ligand)}}{\text{M-(NC-Acid)}} \\ \uparrow & & & & \uparrow \\ & \xrightarrow{+\text{Lewis acid}} & \underset{\text{(isocyanide ligand)}}{\text{M-(CN-Acid)}} & \xrightarrow{\text{isomerization}} & \end{array}$$

Thus the reaction between a transition metal cyanide complex such as $Ru(bipy)_2(CN)_2$ and a Lewis acid like $(CH_3)_3NBH_2I$ might lead to the isolation of either complex, $[Ru(bipy)_2(CNBH_2TMA)_2]I_2$ or $[Ru(bipy)_2(NCBH_2TMA)_2]I_2$ or even a mixture of these products. The identity of the product or products can, however, be inferred from IR spectroscopy (vide supra) if both isomers exist.

To confirm that $(CH_3)_3NBH_2I$ reacts with transition metal cyanides such as $Fe(phen)_2(CN)_2$, $Fe(bipy)_2(CN)_2$ and $Ru(bipy)_2(CN)_2$, to produce complexes with coordinated isocyanide ligands, the two isomers $[Ru(bipy)_2(CNBH_2TMA)_2](PF_6)_2$ and $[Ru(bipy)_2(NCBH_2TMA)_2](PF_6)_2$ were synthesized. These two complexes were chosen because both the ligands, $(CH_3)_3NBH_2NC$ and $(CH_3)_3NBH_2CN$, had been previously prepared and characterized.[33-37] The $(CH_3)_3NBH_2NC$ isomer has a C≡N stretch at 2135 cm^{-1} or some 50 cm^{-1} lower than the C≡N stretch in $(CH_3)_3NBH_2CN$ (ν_{CN} = 2185 cm^{-1}). Thus, $[Ru(bipy)_2(CNBH_2TMA)_2](PF_6)_2$ should have C≡N stretches at lower frequencies than $[Ru(bipy)_2(NCBH_2TMA)_2](PF_6)_2$.

The cyanoborane complex, $[Ru(bipy)_2(NCBH_2TMA)_2](PF_6)_2$, (I), was synthesized from the reaction of $Ru(bipy)_2Cl_2$, $(CH_3)_3NBH_2CN$, and $AgPF_6$ in CH_2Cl_2. This complex had a single broad C≡N stretching frequency of 2215 cm^{-1} in CH_2Cl_2 solution. The reaction of $(CH_3)_3NBH_2I$ with $Ru(bipy)_2(CN)_2$ yielded a product (II), with C≡N stretches at 2133 and 2161 cm^{-1} or an average of 68 cm^{-1} lower than the other

isomer; consistent with the formulation of II as the isocyanoborane complex, $[Ru(bipy)_2(CNBH_2TMA)_2](PF_6)_2$.

The assignment of I as the cyanoborane complex and II as the isocyanoborane complex is supported by both ^1H and ^{11}B NMR spectroscopies based on a comparison of their spectra to the spectra of $(CH_3)_3NBH_2CN$ and $(CH_3)_3NBH_2NC$. Tables 9 and 11 list the ^1H and ^{11}B NMR chemical shifts, respectively, for the complexes I and II in deuterated acetonitrile solutions. Complex I, $[Ru(bipy)_2(NCBH_2TMA)_2](PF_6)_2$, produces a ^{11}B NMR spectrum with a resonance at -26.5 ppm relative to $B(OCH_3)_3$. The proton NMR spectrum of compound I shows a methyl resonance at 2.390 ppm, assignable to the trimethylamine group. By comparison, the resonances of II, $[Ru(bipy)_2(CNBH_2TMA)_2](PF_6)_2$, are found downfield from those of I; with a ^{11}B signal at -32.5 ppm and a methyl resonance in the ^1H NMR spectrum at 2.393 ppm. These values compare favorably with those found in the spectra of the uncomplexed ligands. Trimethylamine cyanoborane, $(CH_3)_3NBH_2CN$, in CD_3CN solution has a ^{11}B resonance at -26.5 ppm and a methyl resonance in the proton NMR at 2.597 ppm. In CD_3CN solution, the resonances of the free, uncomplexed trimethylamine isocyanoborane, $(CH_3)_3NBH_2NC$, are found downfield of its isomer, $(CH_3)_3NBH_2CN$, with a ^{11}B resonance at -32.5 ppm and methyl resonance in the ^1H NMR at 2.659 ppm.

Still further corroboration is found in the UV-VIS spectra and the cyclic voltammograms of the complexes in

acetonitrile solution. The carbon end of the $C\equiv N^-$ ion is known[82] to be more basic than the nitrogen end and thus trimethylamine isocyanoborane is expected to be the stronger field ligand than trimethylamine cyanoborane. An increase in the ligand field strength would stabilize the nonbonding metal orbitals. This would result in the charge-transfer spectrum (UV-VIS) having a lower wavelength of maximum absorbance, λ_{max}, and a cyclic voltammogram with an increased $E_{1/2}$ electrode potential. Tables 1 and 4 list the λ_{max} and the $E_{1/2}$ values respectively for complexes I and II in acetonitrile solution. The isocyanoborane complex II, $[Ru(bipy)_2(CNBH_2TMA)_2](PF_6)_2$, has a λ_{max} of 376 nm and an $E_{1/2}$ of 1.83 V. As expected, the cyanoborane complex I, $[Ru(bipy)_2(NCBH_2TMA)_2](PF_6)_2$, has a higher wavelength of maximum absorbance (λ_{max} = 436 nm) and a lower $E_{1/2}$ ($E_{1/2}$ = 1.41 V) than its isocyanoborane isomer, complex II.

The evidence is clear that the reaction of amine-iodoboranes with the octahedral metal complexes, cis-dicyanobis(1,10-phenanthroline)iron(II), cis-dicyanobis-(2,2'-bipyridine)iron(II), and cis-dicyanobis-(2,2'-bipyridine)ruthenium(II), leads to octahedral amine isocyanoborane metal complexes exclusively and that the cis geometry about the metal ions is preserved in these compounds.

4.2 Properties of Amine Isocyanoborane Complexes

4.2.1 General Properties

The reaction of amine iodoborane compounds with $Fe(phen)_2(CN)_2$, $Fe(bipy)_2(CN)_2$, and $Ru(bipy)_2(CN)_2$ leads to the conversion of the bound cyanide ligands into bound amine isocyanoborane ligands. The coordination of the borane results in a shift in the observed color of the complexes from blue-violet to yellow in the case of the iron complexes and from orange to pale yellow for the ruthenium complexes. The adducts exhibit increased solubilities compared to the starting cyanide complexes. $Fe(phen)_2(CN)_2$, $Fe(bipy)_2(CN)_2$, and $Ru(bipy)_2(CN)_2$ are only slightly soluble in protic solvents such as methanol and less soluble in polar solvents such as methylene chloride or acetonitrile. The isocyanoborane adducts are highly soluble in methylene chloride and acetonitrile, as well as methanol. The last solvent causes eventual decomposition via cleavage of the adducts at the boron and converts the adducts back into the parent cyanide complexes.

The formation of the isocyanide adducts results in increased chemical stability not only at the metal center but also of the borane itself. The complex, $Fe(phen)_2(CN)_2$, is easily oxidized from iron(II) to iron(III) by the action of either nitric acid or perchloric acid.[58] The free ligand, $CNBH_2TMA$, is destructively oxidized by chlorine.[33] However, the isocyanoborane complex, $[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$,

reacts cleanly with chlorine in CH_2Cl_2 solution to yield the iron(II) dichloroisocyanoborane complex, $[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$, in which the CN containing ligand is now $CNBCl_2TMA$.

The isocyanoborane complexes exhibit a wide range of solvolytic stability. The haloisocyanoborane complex, $[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$, can be recrystallized from a refluxing mixture of methanol and acetonitrile while the complex, $[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$, is destroyed overnight by exposure to methanol at room temperature.

4.2.2 Effects of B-N Bond Formation

In all of the isocyanoborane adducts, the formation of the B to N bond (amine-B→N≡C-M) results in profound changes in the properties of both the metal cyanide complex and the amine borane. Evidence of these changes can be found in their respective spectroscopic behaviors as well as their electrochemistry.

As Table 5 clearly shows, the formation of the B-N adduct results in an increase of both C≡N stretching frequencies (νCN_{sym} and νCN_{asym}) by some 75 - 90 cm^{-1} for all of the bis-isocyanoborane complexes $[M-(C\equiv N-B)_2]$ and 40 - 60 cm^{-1} for the cyano-isocyanoborane complexes, $[M-(C\equiv N)(C\equiv N-B)]$, relative to the original cyano complexes, $[M-(C\equiv N)_2]$. This is to be expected since CN-B σ bond formation would remove electron density from the nominally antibonding σ^*_s orbital (see Figure 12) leading to a strengthening of the C≡N bond.[83]

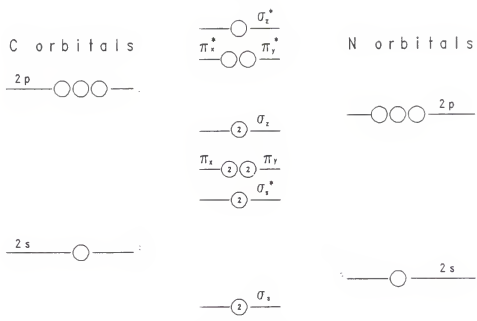

Figure 12. MO diagram for CN^- ion (with the number of electrons in each MO in the circle).

The shift in the stretching frequencies, νCN_{sym} and νCN_{asym}, are somewhat moderated by the strength of the amine bound to the boron (M-C≡N-BH_2-Amine). A decrease in the amine base strength would increase the effective electronegativity of boron, strengthening the σ_{CN-B} bond, and thus increasing ν_{CN}. The amines used in this study increase in base strength in the order: dimethylamine, 4-picoline, and trimethylamine, as measured by their respective gas phase proton affinities.[84] Figure 13, a plot of the symmetric CN stretching frequency (ν_{sym}) versus the gas phase proton affinity of the amine, clearly shows this trend for the bis isocyanoborane adducts of $Fe(phen)_2(CN)_2$, $Fe(bipy)_2(CN)_2$, and $Ru(bipy)_2(CN)_2$. A similar trend is exhibited by the asymmetric C≡N stretching frequency.

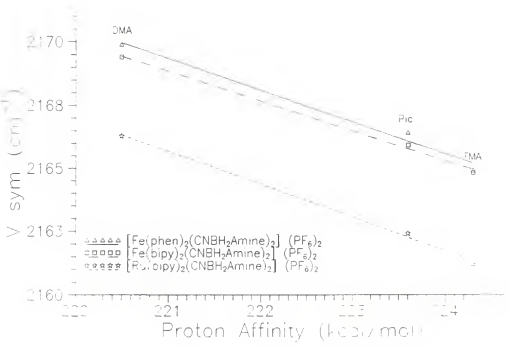

Figure 13. Plot of proton affinity vs. symmetric C≡N stretching frequency.

Other changes produced by B-N bond formation can be found in the UV-VIS spectra. In the complexes studied, the main electronic transitions are aromatic ligand (2,2'-bipyridine or 1,10-phenanthroline) centered π-π^* transitions and metal-to-aromatic ligand charge transfer excitations. The observed UV-VIS absorption wavelength of the charge transfer bands are highly dependent on the relative energies of the occupied metal centered (d_π) orbitals and the ligand centered (π^*) orbitals. Any perturbation of the system introduced by adduct formation that results in a stabilization of the metal orbitals or a destabilization of the ligand π^* orbitals will result in higher energy charge

transfer excitations. The ligand centered π-π^* transitions are relatively unaffected by coordination at the cyanide since any perturbations caused by coordination would tend to shift the energies of the π and π^* orbitals in the same direction. Coordination of a Lewis acid to the nitrogen of a coordinated cyanide ion would increase the π backbonding between the metal d_π orbitals and the cyanide π^* orbitals, thus stabilizing the metal orbitals (see Figure 14).

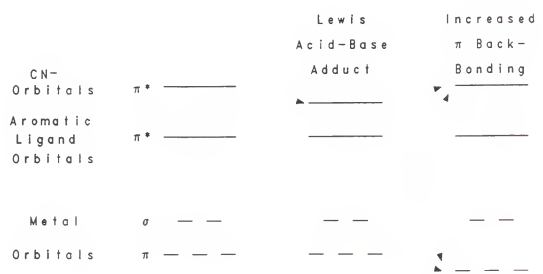

Figure 14. MO diagram for adduct formation.

This stabilization of the metal orbitals results in an increase in the energy difference between the metal π orbitals and the 1,10-phenanthroline or 2,2'-bipyridine π^* orbitals producing a shift to shorter wavelengths for these charge transfer transition. As Table 1 clearly shows, the

coordination of the BH_2-amine cation to the nitrogen end of the coordinated cyanide ion produces such a shift in the charge transfer bands. For the complex, $Fe(phen)_2(CN)_2$, the shift produced by coordination of boron cations to the two cyanide ligands amounts to ≈ 190 nm. The shifts produced in the 2,2'-bipyridine complexes are somewhat less; ≈ 165 nm for the $Fe(bipy)_2(CN)_2$ complex and ≈ 120 nm for the $Ru(bipy)_2(CN)_2$ complexes.

For obvious reasons the changes in the cyanide precursors induced by complexation of the amine-borane cannot be followed by ^{11}B NMR. However, comparison to the free ligands $(CH_3)_3NBH_2NC$ and $(CH_3)_3NBH_2CN$ can be made. Table 11 clearly shows that complexation of the ligands by metal centers results in an upfield shift in their ^{11}B resonances. Like the cyanide stretching frequencies, the ^{11}B NMR chemical shifts of the bis amine-borane adducts correlate with the proton affinities of the amine (see Figure 15). This trend is to be expected as an increase in the proton affinity of the amine would increase the electron density about the boron nucleus, resulting in a less negative ^{11}B NMR chemical shift.

The proton affinities of the amine substituents do not correlate with the proton chemical shifts of the aromatic ligands of the bis amine-borane adducts. The proton affinities increase in the order dimethylamine, 4-picoline, and trimethylamine but, from Table 9, the ^1H chemical shifts of the eight protons on the bidentate aromatic ligands

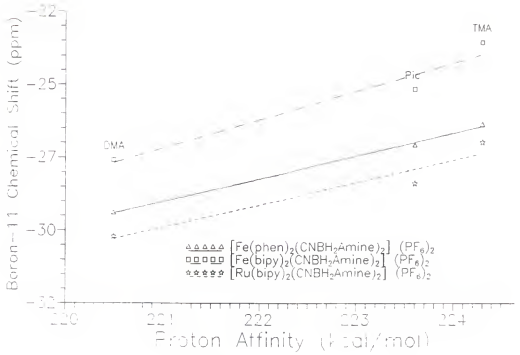

Figure 15. Graph of ^{11}B chemical shift vs. proton affinity.

(1,10-phenanthroline and 2,2'-bipyridine) of the bis amine-borane adducts increase in the order of 4-picoline, dimethylamine, and trimethylamine. Although the variation in chemical shifts is small (about 0.1-0.2 ppm), a trend is clearly discernable. The variation parallels the order of increasing size of the respective amines. This trend is difficult to rationalize.

As inspection of Figures 2 and 3 reveals, the largest of the amines, trimethylamine, would most sterically crowd the "A" protons on the two bidentate ligands resulting in the most deshielded "A" protons. This agrees with the

observed trend. However, an increase in the steric crowding of the "A" protons would also result in an increased tilt of the affected 1,10-phenanthroline or 2,2'-bipyridine ligands away from the trimethylamines, pushing the "A'" protons farther into the π-ring system of the adjacent 2,2'-bipyridine or 1,10-phenanthroline ligands. Further penetration of these protons into the adjacent ring would result in increased shielding and a lower chemical shift of the "A'" proton. Thus, the trimethylamine complexes would be expected to have 1,10-phenanthroline and 2,2'-bipyridine ligands with the most shielded "A'" protons and the 4-picoline complexes with the least shielded "A'" protons. This is backwards of the observed trend. Apparently, the inductive effects of the coordinated amine are not being effectively transmitted to the bidentate ligands.

Finally, the effects of B-N bond formation are clearly evident in the electrochemical behavior of these complexes. The $E_{\frac{1}{2}}$ values for the $M^{+3/+2}$ couples are listed in Table 4 and indicate that the redox potentials are greatly dependent on the number of isocyanoborane ligands formed.

As mentioned earlier, coordination of a Lewis acid at the nitrogen end of a cyanide ligand increases the π-back-bonding between the metal and the cyanide ligand resulting in a stabilization of the filled metal d_π orbitals (see Figure 14). Removal of an electron (oxidation) from the adduct would, therefore, require a higher potential than from the nonadducted cyanide compound. This effect would be

cumulative; the greater the number of adducts the higher the resulting electrode potential. Figure 16 shows the sizable increase in the metal centered electrode potentials which occurs as the number of amine-borane cations which are coordinated to cyanide ligands increases. This amounts to an increase of approximately 0.44 V per borane cation coordinated for both the ruthenium and iron complexes.

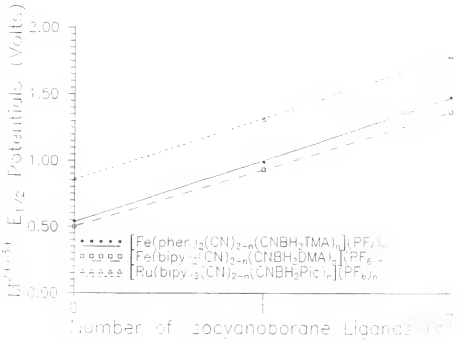

Figure 16. Plot of electrode potential ($E_{\frac{1}{2}}$) versus the number of amine-borane cations coordinated to the cyanide ligands.

4.2.3 Effects of Halogenation

Chlorination and bromination of the isocyanoborane ligands of $[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$ results in the replacement of the hydrogen atoms attached to boron with the

respective halogen atoms. This replacement of the hydrogen results in an increase in the effective electronegativity of the boron and all of the expected orbital energy changes discussed above. Since halogenation results in increased backbonding between the isocyanoborane ligand and the metal center, the d_{π}-π^* transitions in the halogenated complexes lie at higher energy (lower λ) than the nonhalogenated analog. These transitions occur at 368 nm for both, $[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$ and $[Fe(phen)_2(CNBBr_2TMA)_2](PF_6)_2$.

In a similar vein, the increased backbonding results in a stabilization of the metal d_{π} orbitals and consequently, oxidation of the electron from these orbitals is more difficult. Thus, halogenation of isocyanoborane complexes increases the $M^{+3/+2}$ electrode potentials. In the case of $[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$, this increase in $E_{\frac{1}{2}}$ value is 0.26 V or an average of 0.06 V per halogen atom substituted.

Finally, as halogen atoms are more electron withdrawing than hydrogen, the halogenation of the boron also results in a net deshielding of the boron. The effect of deshielding can be found in the ^{11}B NMR spectrum of $[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$. The ^{11}B resonance for this compound is found at -17.8 ppm. This resonance, as expected, is downfield (by 8.1 ppm) from $[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$.

CHAPTER 5

SUMMARY

The synthesis of bound amine isocyanoborane ligands is facile. Amine iodoboranes react cleanly with cyano complexes, such as $Fe(phen)_2(CN)_2$, $Fe(bipy)_2(CN)_2$, and $Ru(bipy)_2(CN)_2$, to yield ionic iodide complexes containing amine isocyanoborane ligands bonded to the metal centers. The iodide salts can be converted into the corresponding hexafluorophosphate salts by the action of aqueous NH_4PF_6 or $AgPF_6$ in acetonitrile. The isocyanoborane adducts show a marked increase in solubility in both polar protic and aprotic solvents over the parent cyano complexes.

The coordination of amine isocyanoboranes to metal centers affects the properties of the isocyanoborane ligand. The ^{11}B resonance and the CH_3 resonance in the ^1H NMR are found downfield (in more deshielded positions) from the signals of the uncomplexed ligand. The positions of the boron resonances are also dependent upon the strength of the amine bases coordinated to the boron in the amine isocyanoborane ligand and correlate with the gas phase proton affinities.

More importantly, adduct formation alters the environment of the metal center. The formation of the CN-B

bond increases the π-acceptor ability of the CN moiety thereby increasing the π backbonding between the metal ion and the CN ligand. Consequently, the bis-isocyanoborane adducts have higher $E_{\frac{1}{2}}$ electrode potentials by approximately 0.9 V than the corresponding cyano complexes. In fact, in the cases of $Fe(phen)_2(CN)_2$, $Fe(bipy)_2(CN)_2$, and $Ru(bipy)_2(CN)_2$ the potentials are raised to the point where elemental chlorine cannot induce oxidation of the metal ions to the +3 states. The redox potential can be raised further by halogenation of the borane. In the case of $[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$, substitution of the hydrogens of the borane by chlorination further increases the electrode potential by 0.26 V. The formation of CN-B bond also results in a hypsochromic shift of the charge transfer absorption band in the UV-VIS spectrum by $\approx$ 190 nm for $Fe(phen)_2(CN)_2$, $\approx$ 165 nm for $Fe(bipy)_2(CN)_2$, and $\approx$ 120 nm for $Ru(bipy)_2(CN)_2$.

Thus, amine isocyanoboranes, like organo-isonitriles to which they are structurally and electronically similar, can be used to alter the electronic environment in metal complexes. However, the use of amine isocyanoboranes offer several potential advantages over organo-isonitriles. Firstly, the ligand need not be synthesized prior to use, but instead, can be synthesized <u>in situ</u> from an amine iodoborane and a cyanide ion already coordinated to the metal. Secondly, this adduct formation can be reversed by solvolysis which cleaves the borane and leaves behind the

original cyanide ion. Finally, the amine isocyanoborane can be derivatized more easily than organo-isonitrile. The reaction with halogens results in substitution at the boron. And, by further derivatization at the boron center, such as changes in coordination number and charge on the ligand, it should be possible to synthesize a nearly endless variety of boron isocyanide ligands.

APPENDIX A

INFRARED SPECTRA

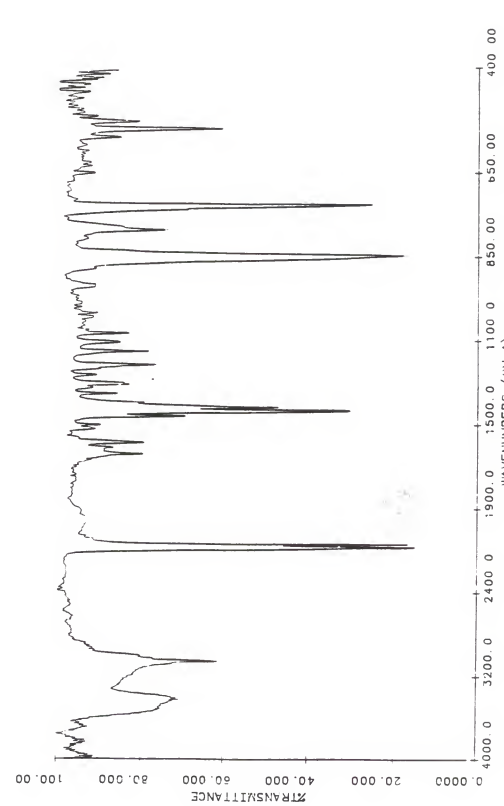

Figure A1. IR Spectrum of $Fe(phen)_2(CN)_2$ in KBr.

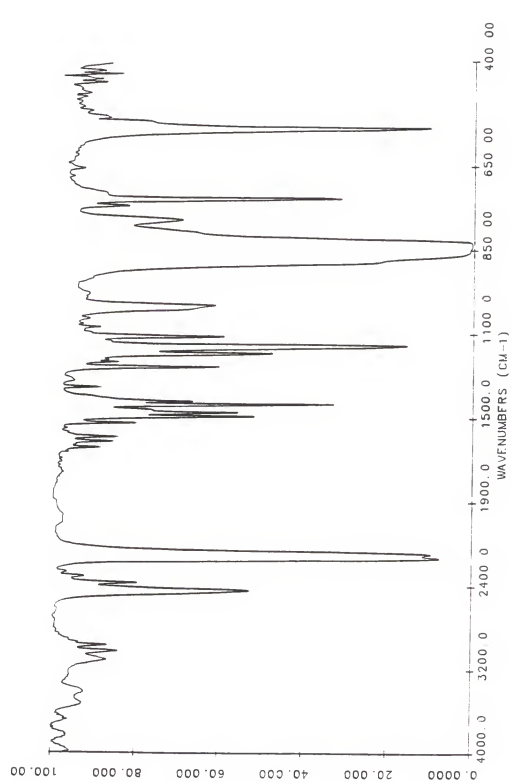

Figure A2. IR Spectrum of $[Fe(phen)_2(CNBH_2TMA)_2](PF_6)_2$ in KBr.

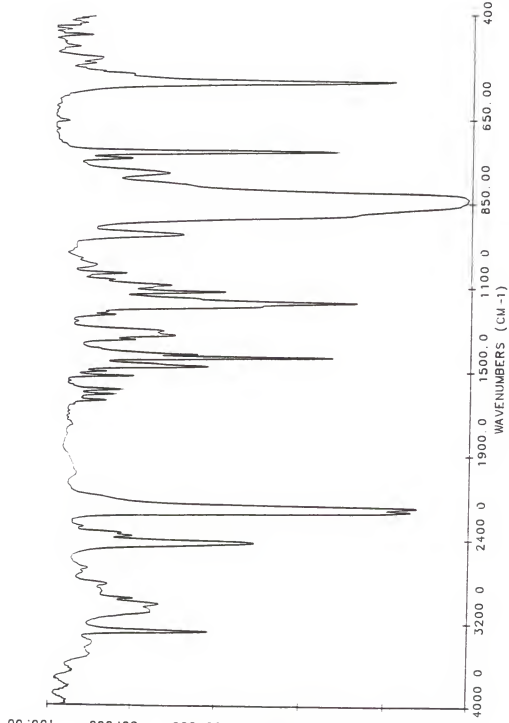

Figure A3. IR Spectrum of $[Fe(phen)_2(CNBH_2DMA)_2](PF_6)_2$ in KBr.

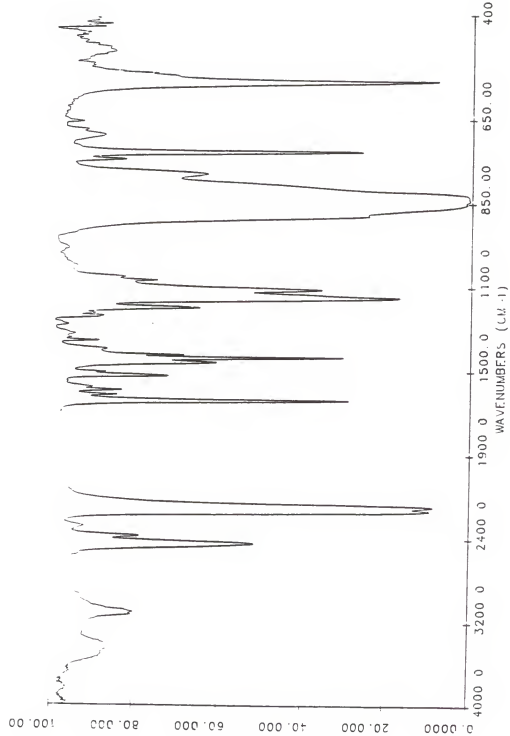

Figure A4. IR Spectrum of $[Fe(phen)_2(CNBH_24\text{-}Pic)_2](PF_6)_2$ in KBr.

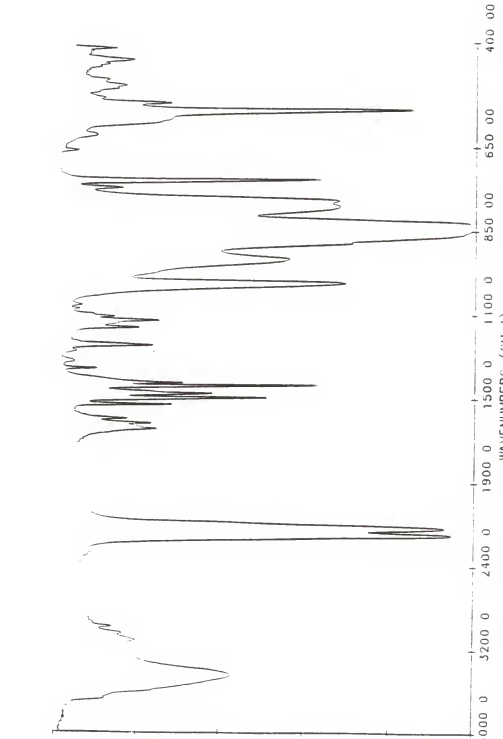

Figure A5. IR Spectrum of $[Fe(phen)_2(CNBCl_2TMA)_2](PF_6)_2$ in KBr.

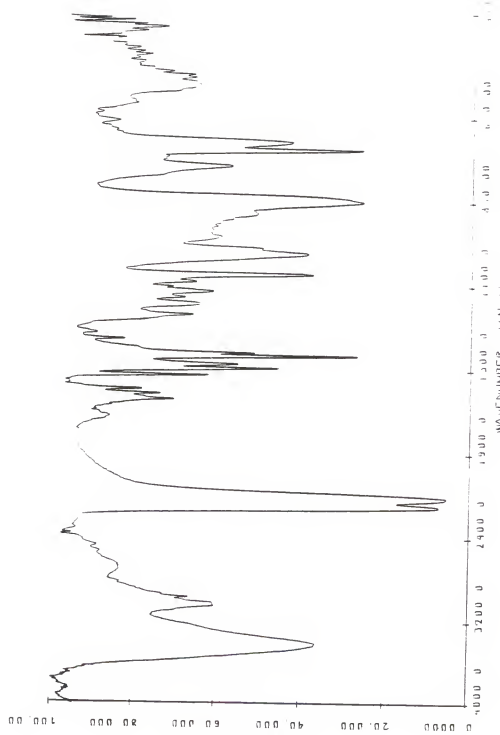

Figure A6. IR Spectrum of $[Fe(phen)_2(CNBBr_2TMA)_2](PF_6)_2$ in KBr.

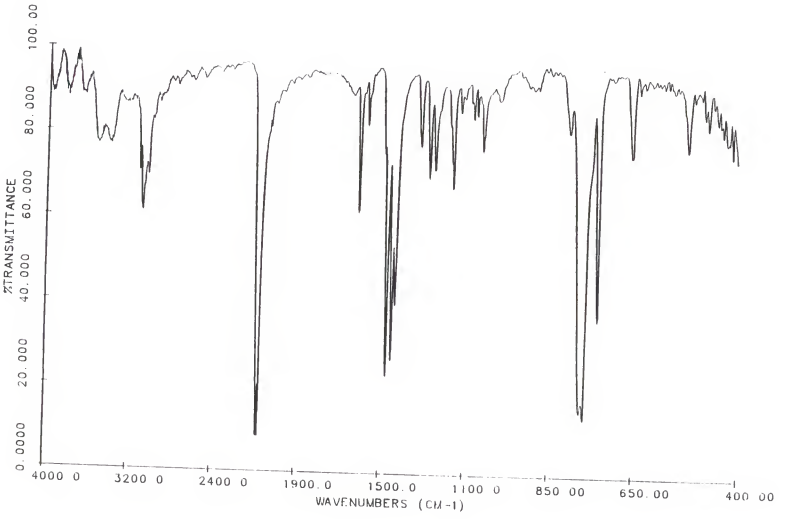

Figure A7. IR Spectrum of $Fe(bipy)_2(CN)_2$ in KBr.

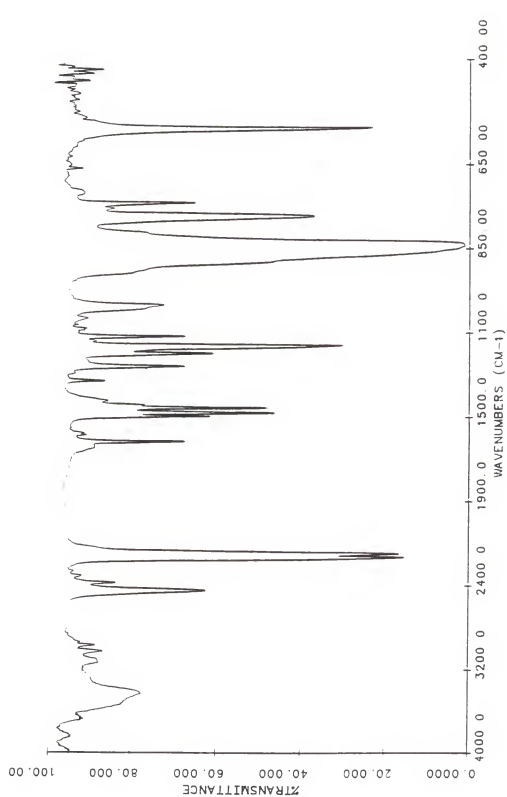

Figure A8. IR Spectrum of $[Fe(bipy)_2(CNBH_2TMA)_2](PF_6)_2$ in KBr.

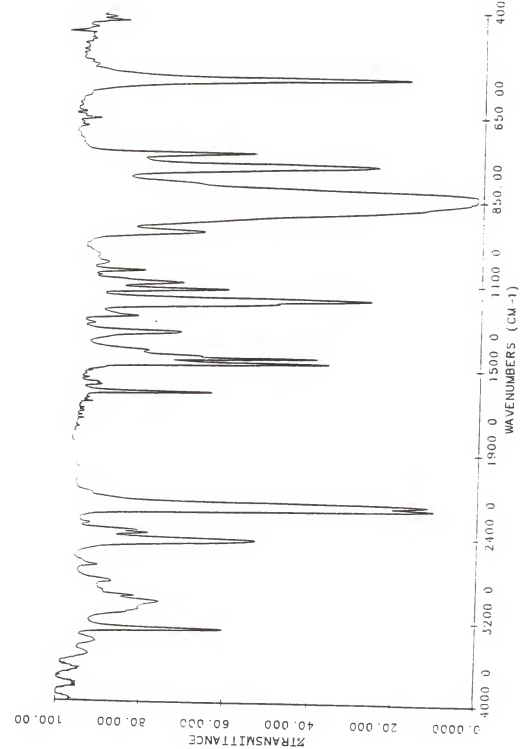

Figure A9. IR Spectrum of $[Fe(bipy)_2(CNBH_2DMA)_2](PF_6)_2$ in KBr.

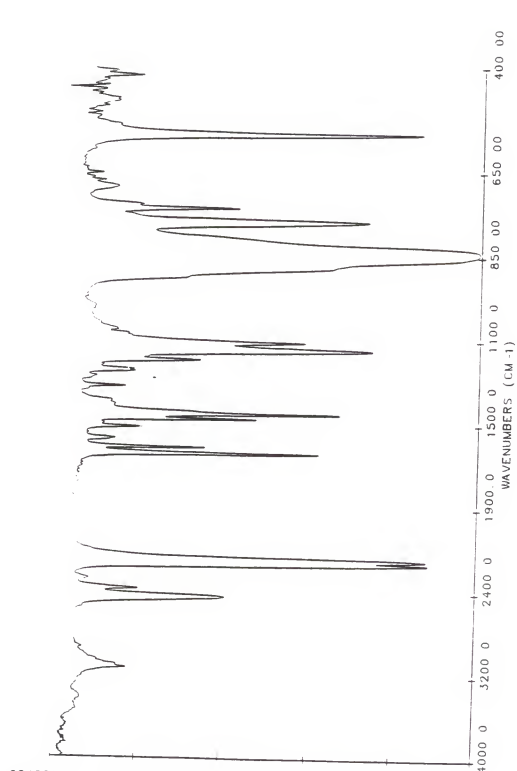

Figure A10. IR Spectrum of $[Fe(bipy)_2(CNBH_24\text{-}Pic)_2](PF_6)_2$ in KBr.

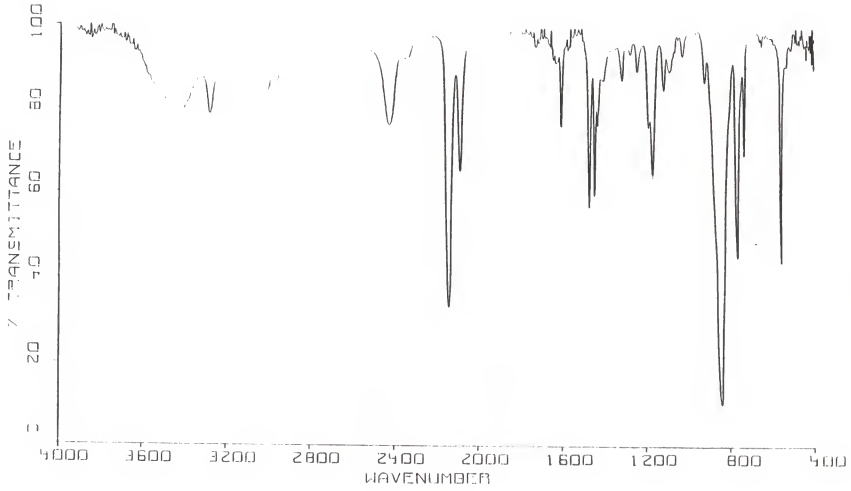

Figure A11. IR Spectrum of $[Fe(bipy)_2(CN)(CNBH_2DMA)](PF_6)$ in KBr.

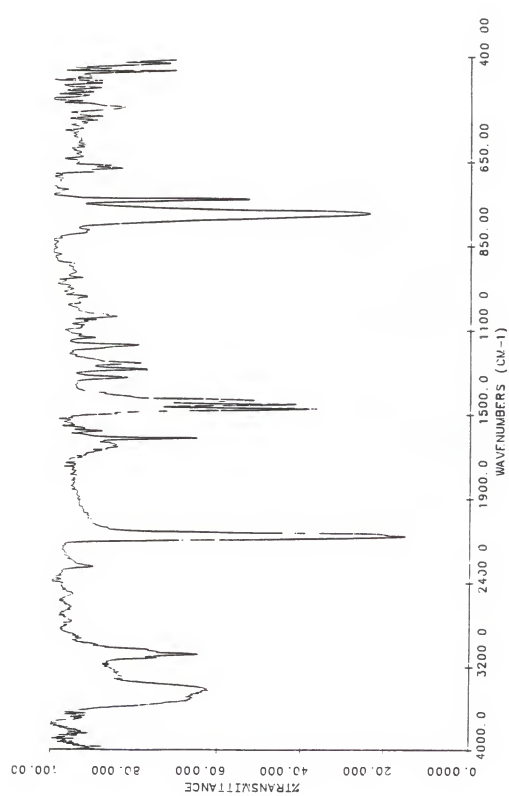

Figure A12. IR Spectrum of $Ru(bipy)_2(CN)_2$ in KBr.

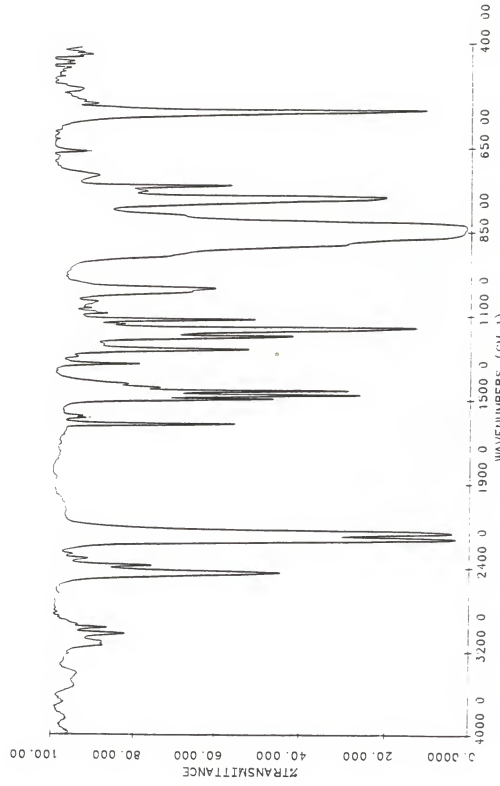

Figure A13. IR Spectrum of $[Ru(bipy)_2(CNBH_2TMA)_2](PF_6)_2$ in KBr.

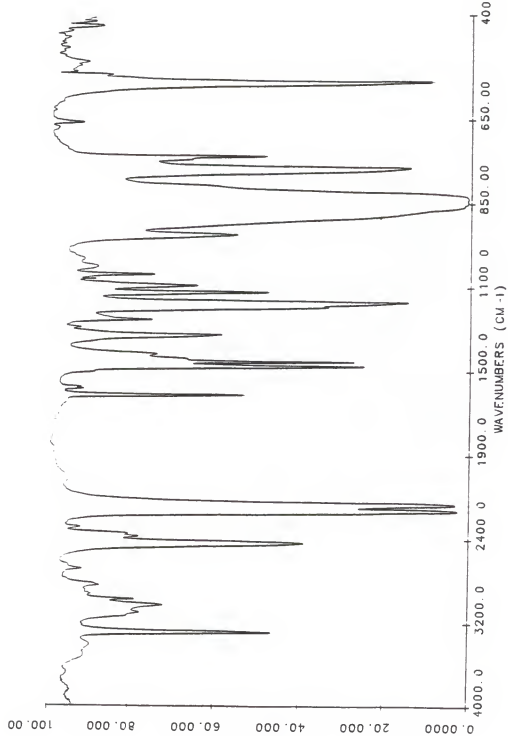

Figure A14. IR Spectrum of $[Ru(bipy)_2(CNBH_2DMA)_2](PF_6)_2$ in KBr.

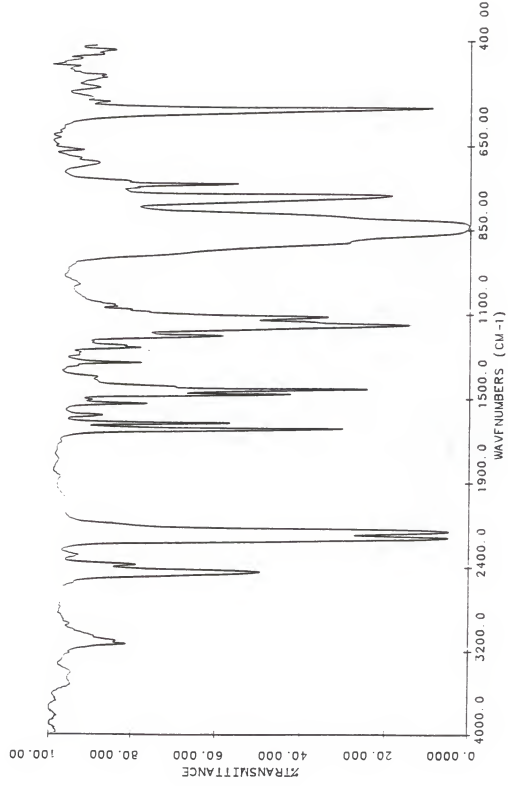

Figure A15. IR Spectrum of $[Ru(bipy)_2(CNBH_24\text{-}Pic)_2](PF_6)_2$ in KBr.

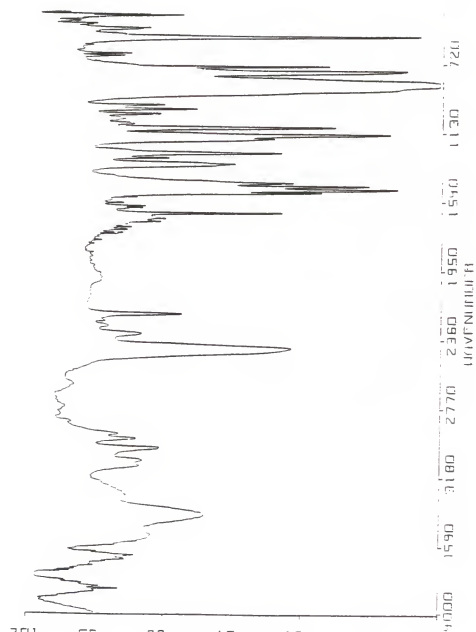

Figure A16. IR Spectrum of $[Ru(bipy)_2(\underline{NC}BH_2TMA)_2](PF_6)_2$ in KBr.

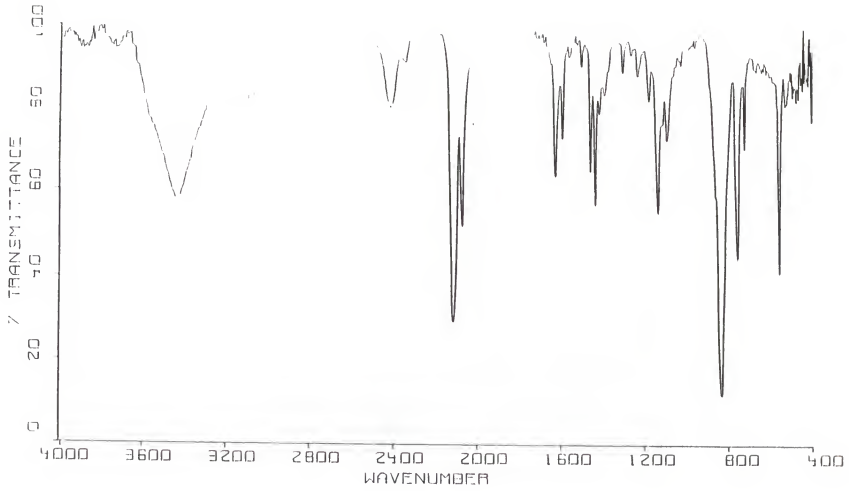

Figure A17. IR Spectrum of $[Ru(bipy)_2(CN)(CNBH_2 4\text{-}Pic)](PF_6)$ in KBr.

APPENDIX B

ULTRAVIOLET-VISIBLE SPECTRA

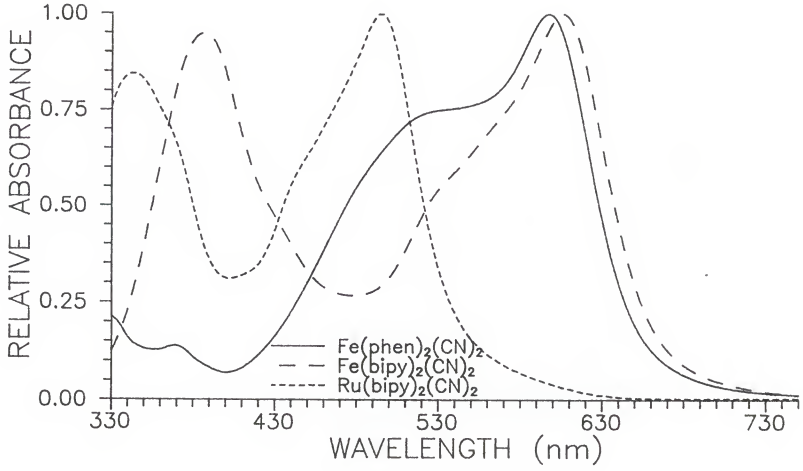

Figure B1. UV-VIS Spectrum of $Fe(phen)_2(CN)_2$, $Fe(bipy)_2(CN)_2$, and $Ru(bipy)_2(CN)_2$ in acetonitrile solution from 330-750 nm.

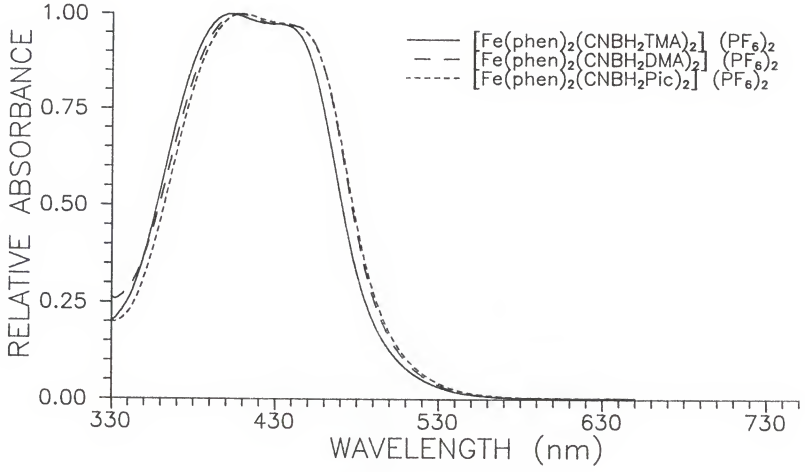

Figure B2. UV-VIS Spectrum of $Fe(phen)_2(CNBH_2TMA)_2(PF_6)_2$, $Fe(phen)_2(CNBH_2DMA)_2(PF_6)_2$, and $Fe(phen)_2(CNBH_2Pic)_2(PF_6)_2$, in acetonitrile solution from 330-750 nm.

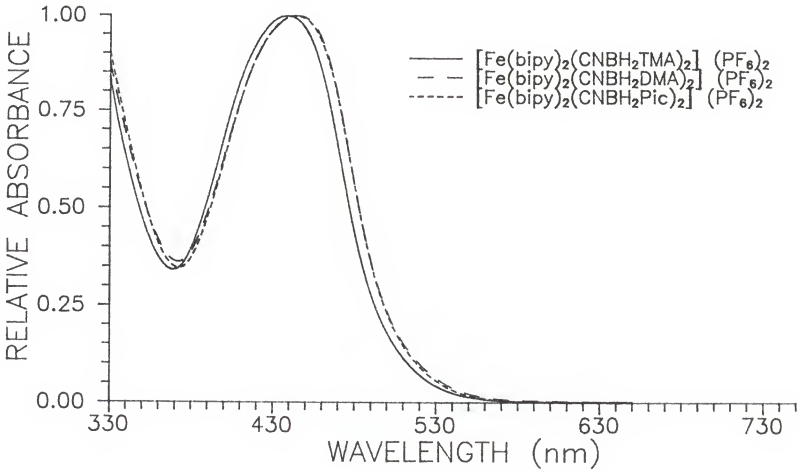

Figure B3. UV-VIS Spectrum of $Fe(bipy)_2(CNBH_2TMA)_2(PF_6)_2$, $Fe(bipy)_2(CNBH_2DMA)_2(PF_6)_2$, and $Fe(bipy)_2(CNBH_2Pic)_2(PF_6)_2$, in acetonitrile solution from 330-750 nm.

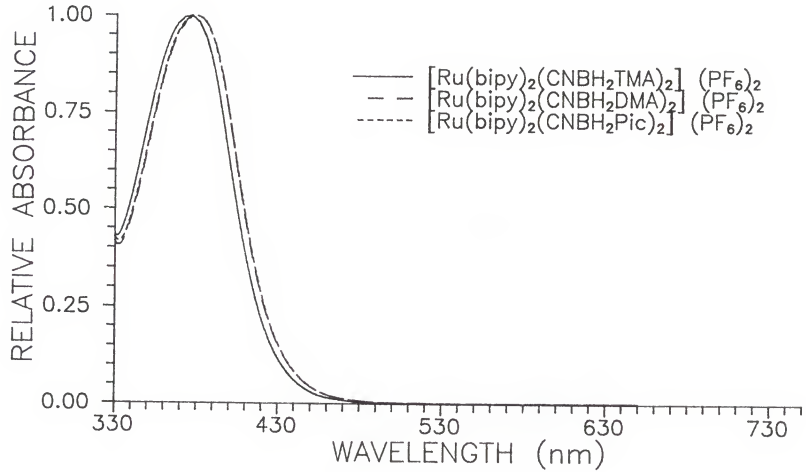

Figure B4. UV-VIS Spectrum of $Ru(bipy)_2(CNBH_2TMA)_2(PF_6)_2$, $Ru(bipy)_2(CNBH_2DMA)_2(PF_6)_2$, and $Ru(bipy)_2(CNBH_2Pic)_2(PF_6)_2$, in acetonitrile solution from 330-750 nm.

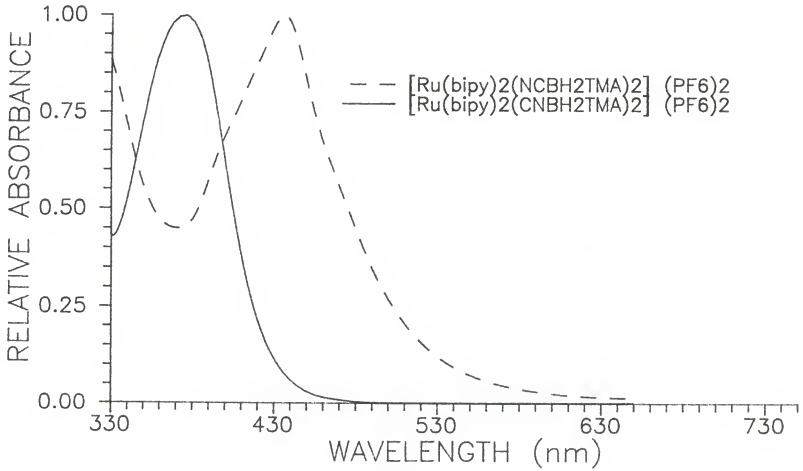

Figure B5. UV-VIS Spectrum of $Ru(bipy)_2(\underline{NC}BH_2TMA)_2(PF_6)_2$ and $Ru(bipy)_2(\underline{CN}BH_2TMA)_2(PF_6)_2$ in acetonitrile solution from 330-750 nm.

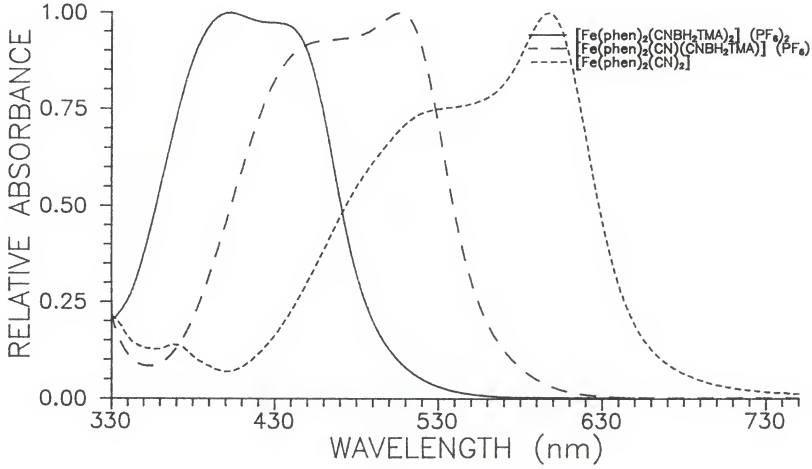

Figure B6. UV-VIS Spectrum of $Fe(phen)_2(CNBH_2TMA)_2(PF_6)_2$, $Fe(phen)_2(CN)(CNBH_2TMA)(PF_6)$, and $Fe(phen)_2(CN)_2$ in acetonitrile solution from 330-750 nm.

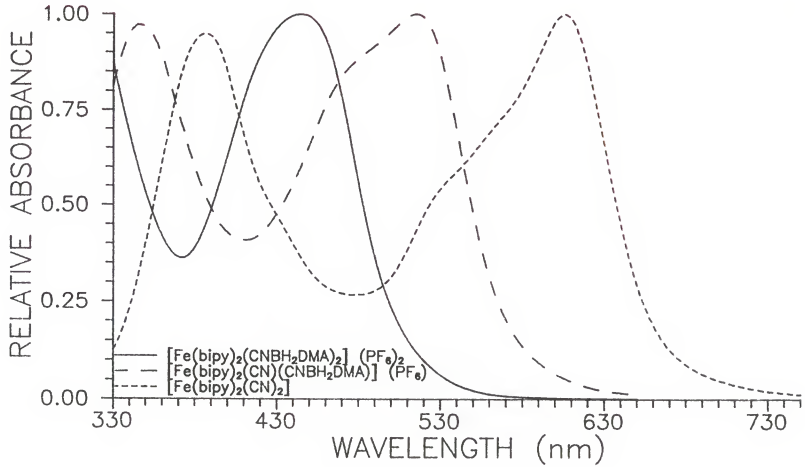

Figure B7. UV-VIS Spectrum of $Fe(bipy)_2(CNBH_2DMA)_2(PF_6)_2$, $Fe(bipy)_2(CN)(CNBH_2DMA)(PF_6)$, and $Fe(bipy)_2(CN)_2$ in acetonitrile solution from 330-750 nm.

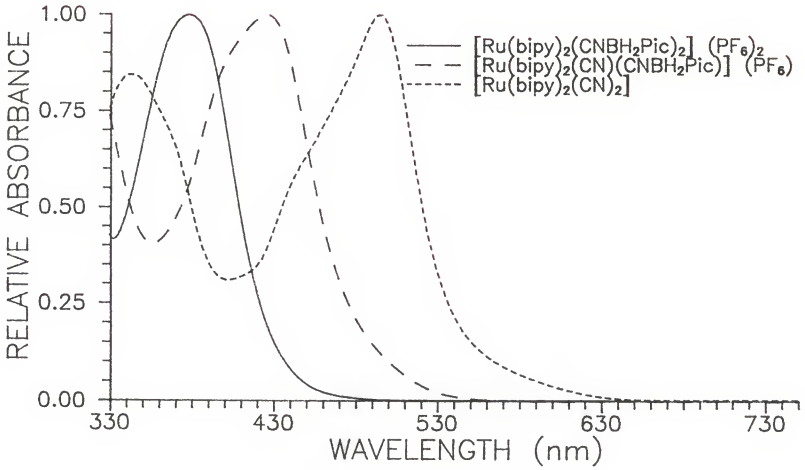

Figure B8. UV-VIS Spectrum of $Ru(bipy)_2(CNBH_2Pic)_2(PF_6)_2$, $Ru(bipy)_2(CN)(CNBH_2Pic)(PF_6)$, and $Ru(bipy)_2(CN)_2$ in acetonitrile solution from 330-750 nm.

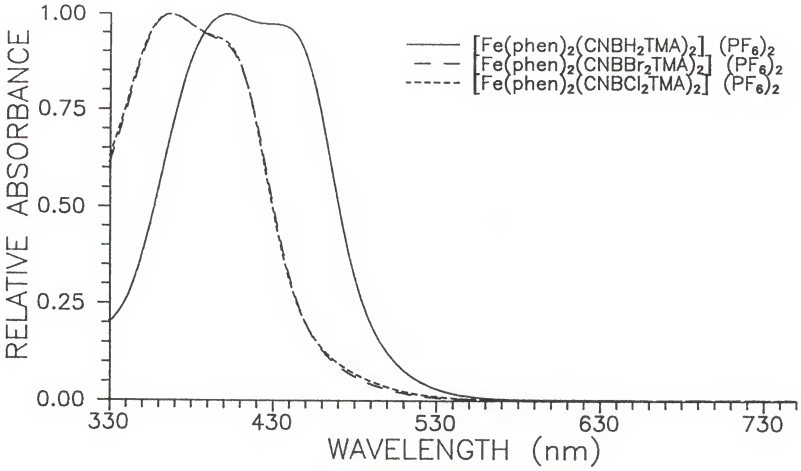

Figure B9. UV-VIS Spectrum of $Fe(phen)_2(CNBH_2TMA)_2(PF_6)_2$, $Fe(phen)_2(CNBBr_2TMA)_2(PF_6)_2$, and $Fe(phen)_2(CNBCl_2TMA)_2(PF_6)_2$, in acetonitrile solution from 330-750 nm.

REFERENCES

1. Lieke, W. Justus Liebigs Ann. Chem. **1859**, 112, 316.

2. Meyer, E. J. Prakt. Chem. **1866**, 67, 147.

3. Gautier, A. Justus Liebigs Ann. Chem. **1867**, 14, 289.

4. Gautier, A. Justus Liebigs Ann. Chem. **1869**, 146, 119.

5. Hofmann, A. W. Justus Liebigs Ann. Chem. **1867**, 144, 114.

6. Ugi, I., Isonitrile Chemistry, Academic Press, New York, **1971**.

7. Malatesta, L.; Bonati, F., Isocyanide Complexes of Metals, John Wiley and Sons, London, **1969**.

8. Treichel, P. M. Adv. Organomet. Chem. **1973**, 11, 21.

9. Cotton, F. A.; Wilkinson, G., Advanced Inorganic Chemistry, 4th Ed., John Wiley and Sons, New York, **1980**.

10. Guy, M. P.; Coffer, J. L.; Rommel, J. S.; Bennett, D. W. Inorg. Chem. **1988**, 27, 2942.

11. Purcell, K.F. J. Am. Chem. Soc. **1969**, 91, 3487.

12. Glidewell, C. Inorg. Chim. Acta **1974**, 11, 257.

13. Shriver, D. F. Structure and Bonding **1966**, 1, 32.

14. Lappert, M. F.; Pyzora, H. Adv. Inorg. Chem. Radiochem. **1966**, 9, 133.

15. Müller, J.; Schmock, F.; Klopsch, A.; Dehnicke, K. Chem. Ber. **1975**, 108, 664.

16. Dehnicke, K.; Wilson, I.L. J. Chem. Soc., Dalton Trans. **1973**, 1428.

17. Weller, F.; Wilson, I.L.; Dehnicke, K. J. Organometal. Chem. **1971**, 30, C1.

18. Weller, F.; Dehnicke, K. J. Organometal. Chem. **1972**, 36, 23.

19. Ehemann, T.; Dehnicke, K. J. Organometal. Chem. **1974**, 64, C33.

20. Ehemann, T.; Dehnicke, K. J. Organometal. Chem. **1974**, 71, 191.

21. McBride, J. J.; Beachell, H. C. J. Am. Chem. Soc. **1952**, 74, 5247.

22. Seyferth, D.; Kahlen, N. J. Org. Chem. **1960**, 25, 809.

23. Thayer, J. S.; West, R. Adv. Organomet. **1967**, 5, 169.

24. Bither, T.A.; Knoth, W.H.; Lindsey Jr., R.V.; Sharkey, W.H. J. Am. Chem. Soc. **1968**, 80, 4151.

25. Bürger, H.; Schirawski, G. Spectrochim. Acta **1971**, 27A, 159.

26. Booth, M.R.; Frankiss, S.G. Spectrochim. Acta **1970**, 26A, 859.

27. Secker, J.A.; Thayer, J.S. Inorg. Chem. **1975**, 14, 573.

28. Booth, J.A.; Frankiss, S.G. Spectroscopic Methods in Organometallic Chemistry, George, W.O., Ed., Butterworth, London **1970**, p. 200.

29. Durig, J.R.; Li, Y.S.; Turner, J.B. Inorg. Chem. **1974**, 13, 1495.

30. Silverstein, R. M., Bassler, G. C., and Morrill, T. C. Spectrometric Identification of Organic Compounds 4th Ed. John Wiley and Sons, New York **1981.**

31. Conley, R. T. Infrared Spectroscopy, Allyn and Bacon, Inc., Boston, **1972.**

32. Wade, R. C.; Sullivan, E. A.; Bersheid, J. R. Jr.; Purcell, K.F. Inorg. Chem. **1970**, 9, 2146.

33. Vidal, J. L. Ph. D. Dissertation, University of Florida, 1974.

34. Vidal, J. L.; Ryschkewitsch, G. E. Inorg. Chem. **1977**, 16, 1898.

35. Vidal, J. L.; Ryschkewitsch, G. E. Inorg. Syn. **1979**, 19, 223.

36. Uppal, S. S.; Kelly, H. C. Chem. Comm. **1970**, 1619.

37. Weidig, C.; Uppal, S. S.; Kelly, H. C. Inorg. Chem. **1974**, 13, 1763.

38. Vidal, J. L.; Ryschkewitsch, G. E. J. Inorg. Chem. Nucl. Chem. **1977**, 39, 1097.

39. Vidal, J. L.; Ryschkewitsch, G. E. Chem. Comm. **1976**, 192.

40. Shriver, D. F. J. Am. Chem. Soc. **1963**, 85, 1405.

41. Rupp, J. J.; Shriver, D. F. Inorg. Chem. **1967**, 6, 755.

42. Kristoff, J. S.; Shriver, D. F. Inorg. Chem. **1973**, 12, 1738.

43. Manzer, L. E.; Seidel, W. C. J. Am. Chem. Soc. **1975**, 97, 1956.

44. Manzer, L. E.; Anton, M. F. Inorg. Chem. **1977**, 16, 1229.

45. Purcell, K. F.; Yeh, S.M.; Eck, J. S. Inorg. Chem. **1977**, 16, 1708-1715.

46. Ryschkewitsch, G. E.; Mathur, M. A. J. Inorg. Nucl. Chem. **1979**, 41, 1563.

47. Höfler, M.; Löwenich, H. J. Organomet. Chem. **1982**, 226, 229.

48. W. L. Jolly, The Synthesis and Characterization of Inorganic Compounds, Prentice-Hall Inc., Englewood Cliffs, N. J., **1970**.

49. Ryschkewitsch, G. E.; Wiggins, J. W. Inorg. Syn. **1970**, 12, 120.

50. Wisian-Neilson, P.; Das, M. K.; Spielvogel, B. F. Inorg. Chem. **1978**, 17, 2327.

51. Quattro Pro Version 1.00, Borland International, Inc., 1800 Greenhills Road, P.O. Box 660001, Scotts Valley, CA. 95066-0001.

52. Grapher Version 1.75, Golden Software, P.O. Box 281, Golden, CO. 80402.

53. Akabori, K.; Matsuo, H.; Yamamoto, Y. J. Inorg. Nucl. Chem. **1973**, 35, 2679.

54. Baker, W. A.; Bobinich, H. M. Inorg. Chem. **1963**, 2, 1071.

55. Madeja, K.; Wilke, W.; Schmidt, S. Z. Anorg. Chem. **1966**, 346, 306.

56. Lay, P. A.; Sargeson, A. M.; Taube, H. Inorg. Syn. **1986**, 24, 291-299.

57. Personal communication Dr. E. F. Stine,

58. Schilt, A. A. J. Am. Chem. Soc. **1960**, 82, 3000; Schilt, A. A. Inorg. Syn. **1970**, 12, 247

59. Madeja, K.; König, E. J. Inorg. Nucl. Chem. **1963**, 25, 337.

60. Demas, J. N.; Turner, T. F. ; Crosby, G. A. Inorg.Chem. **1969**, 8, 674.

61. White, G. M.; Ohnesorge, W. E. J. Inorg. Nucl. Chem. **1972**, 34, 1453.

62. McKenzie, E. D. Coord. Chem. Rev. **1971**, 6, 187-217.

63. Smith, G.; O'Reilly, E.J.; Kennard, C. H. L.; White, A. J.Chem.Soc. Dalton Trans. 1977, 1184-1190.

64. Atwood, J. L.; Simms, M.L.; Zatko, D. A. Cryst. Struct. Commun. **1972**, 2, 279-82.

65. Nakai, H. Bull. Chem. Soc. Jpn. **1971**, 44, 2412-2415.

66. Ferrari, M. B.; Fava, G. G.; Pelizzi, C. J. Chem. Soc. Chem. Commun. **1977**, 8-9.

67. Grdenić, D.; Kamenar, B.; Hergold-Brundić, A. Cryst. Struct Commun. **1978**, 7, 245-250.

68. Chieh, P. C. J. Chem. Soc. Dalton Trans. **1972**, 1643-1646.

69. Hinamotto, M.; Ooi, S.; Kuraya, H. J. Chem. Soc. Chem. Commun. **1972**, 356-357.

70. Rund, J. V.; Hazell, A. C. Acta Cryst. **1980**, B36, 3103-3105.

71. Dong, V.; Endres, H.; Keller, H. J.; Moroni, W.; Nöthe, D. Acta Cryst. **1978**, B33, 2428-2431.

72. Endres, H.; Keller, H. J.; Moroni, W., Nöthe, D.; Dong, V. Acta Cryst. **1978**, B34, 1823-1827.

73. Hazell, A.; Mukhopadhyay, A. Acta Cryst. **1980**, B36, 1647-1649.

74. Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. J. Am. Chem. Soc. **1980**, 102, 600-607.

75. Che, C. M.; Wong, K. Y.; Leung, W. H.; Poon, C. K. Inorg. Chem. **1986**, 25, 345-348.

76. Dobson, J. C.; Takeuchi, K. J.; Pipes, D. W.; Geselowitz, D. A.; Meyer, T. J. Inorg. Chem. **1986**, 25, 2357-2365.

77. Farver, O.; Mønsted, O.; Nord, G. J. Am. Chem. Soc. **1979**, 101, 6118-6120.

78. Maddock, A. G. J. Chem. Soc. Dalton Trans. **1986**, 2349-2350.

79. Dove, M. F. A.; Hallett, J. G. J. Chem. Soc. (A) **1969**, 1204-1207.

80. König, E. A. Coordin. Chem. Rev. **1968**, 3, 471-495.

81. Schilt, A. A. Inorg. Chem. **1964**, 3, 1323-1325.

82. Pau, C. F.; Hehre, W. J. J. Phys. Chem. **1982**, 86, 321-322.

83. Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds 3rd Ed. **1978**, J. Wiley and Sons, New York.

84. Aue, D. H. and Bowers, M. T. Gas Phase Chemistry, Vol. 2, Bowers, M. T. Ed., **1979**, Academic Press, New York.

BIOGRAPHICAL SKETCH

Don Scott Swieter was born on March 9, 1955 in Ypsilanti, Michigan. After attending nine different schools located throughout the world, Don graduated from Fort Pierce Central High School in Fort Pierce, Florida, in June of 1973. That September he entered Florida Atlantic University as a Faculty Scholar and graduated with a Bachelor of Science degree in chemistry in August, 1976. From September, 1976, until the present time he has pursued his graduate work towards a Doctor of Philosophy degree in the Chemistry at the University of Florida. In August, 1983, he became a member of the faculty at Santa Fe Community College where he is currently a tenured instructor of chemistry.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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